UNIVERSIDADE FEDERAL DO PARANÁ

HUGO SARMIENTO VELA

THE NEW ANALYTICAL METHODOLOGY OF THERMAL DESORPTION USING PASSIVE SAMPLING FOR BTEX

CURITIBA

2019

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Dissertação apresentada ao curso de Pós-Graduação em Engenharia de Recursos Hídricos e Ambiental PPGERHA, Setor de Tecnologia da Universidade Federal do Paraná, como requisito parcial à obtenção do título de Mestre em Engenharia de Recursos Hídricos e Ambiental.
Orientador: Professor Dr. Ricardo H. M. Godoi.

CURITIBA
2019

Catalogação na Fonte: Sistema de Bibliotecas, UFPR
Biblioteca de Ciência e Tecnologia

V432n Vela, Hugo Sarmiento
The new analytical methodology of thermal desorption using passive sampling for BTEX [recurso eletrônico] / Hugo Sarmiento Vela. – Curitiba, 2019.

Tese - Universidade Federal do Paraná, Setor de Tecnologia, Programa de Pós-Graduação em Engenharia de Recursos Hídricos e Ambiental, 2019.

Orientador: Ricardo Henrique Moreton Godoi .

1. Dessorção térmica. 2. Dispositivos de amostragem passiva. 3. Cromatografia a gás. 4. BTEX (Benzene, Toluene, Etilbenzene and Xylenes). 5. Validação, Técnica de . I. Universidade Federal do Paraná. II. Godoi, Ricardo Henrique Moreton. III. Título.

CDD: 543

Bibliotecário: Elias Barbosa da Silva CRB-9/1894

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TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em ENGENHARIA DE RECURSOS HÍDRICOS E AMBIENTAL da Universidade Federal do Paraná foram convocados para realizar a arguição da Dissertação de Mestrado de **HUGO SARMIENTO VELA**, intitulada: **OPTMIZATION OF PASSIVE SAMPLING WITH THERMAL DESORPTION FOR BTEX SAMPLES**, após terem inquirido o aluno e realizado a avaliação do trabalho, são de parecer pela sua Aprovado no rito de defesa.
A outorga do título de Mestre está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

Curitiba, 26 de Abril de 2019.

RICARDO HENRIQUE MORETON GODOI
Presidente da Banca Examinadora

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ATA N° 295

ATA DE SESSÃO PÚBLICA DE DEFESA DISSERTAÇÃO PARA OBTENÇÃO DO GRAU DE MESTRE EM ENGENHARIA DE RECURSOS HÍDRICOS E AMBIENTAL.

No dia vinte e seis de abril de dois mil e dezenove às 13:30 horas, na sala CEHPAR,Centro Politécnico do Setor de Tecnologi do Setor de TECNOLOGIA da Universidade Federal do Paraná, foram instalados os trabalhos de arguição do Mestrando **HUGO SARMIENTO VELA** para a Defesa Pública de sua Dissertação de Mestrado intitulada: **OPTMIZATION OF PASSIVE SAMPLING WITH THERMAL DESORPTION FOR BTEX SAMPLES**. A Banca Examinadora, designada pelo Colegiado do Programa de PósGraduação em ENGENHARIA DE RECURSOS HÍDRICOS E AMBIENTAL da Universidade Federal do Paraná, foi constituída pelos seguintes Membros: RICARDO HENRIQUE MORETON GODOI (UFPR), ARION ZANDONÁ FILHO (UFPR-PPGEQ), HELOISE GARCIA KNAPIK (UFPR). Dando início à sessão, a presidência passou a palavra a(o) discente, para que o mesmo expusesse seu trabalho aos presentes. Em seguida, a presidência passou a palavra a cada um dos Examinadores, para suas respectivas arguições. O aluno respondeu a cada um dos arguidores. A presidência retomou a palavra para suas considerações finais. A Banca Examinadora, então, e, após a discussão de suas avaliações, decidiu-se pela Aprovar do aluno. O Mestrando foi convidado a ingressar novamente na sala, bem como os demais assistentes, após o que a presidência fez a leitura do Parecer da Banca Examinadora. A aprovação no rito de defesa deverá ser homologada pelo Colegiado do programa, mediante o atendimento de todas as indicações e correções solicitadas pela banca dentro dos prazos regimentais do programa. A outorga do título de Mestre está condicionada ao atendimento de todos os requisitos e prazos determinados no regimento do Programa de Pós-Graduação. Nada mais havendo a tratar a presidência deu por encerrada a sessão, da qual eu, **RICARDO HENRIQUE MORETON GODOI**, lavrei a presente ata, que vai assinada por mim e pelos membros da Comissão Examinadora.

Observações: Segue a data para a colocação do trabalho acima. O novo título é: The New analytical methodology for Thermal Desorption using passive sampling for BTEX.

Curitiba, 26 de Abril de 2019.

RICARDO HENRIQUE MORETON GODOI
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ARION ZANDONÁ FILHO
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I dedicate this work to my family, especially to my father who looks at me from heaven, to my mother who has always been with me, my wife and my children who accompany me in the distance.

ACKNOWLEDGEMENTS

God for accompanying me and give me the strength not to desist.

To Professor Ricardo Godoi for supporting and valuing my work and for the effort to make this research go forward and for its guidance.

To my son Andrés David for being besides my son, the person who really listens to me.

To my mother for supporting me unconditionally and to my father who would be very proud to see another of his children postgraduate.

To my wife and my son Diego Alejandro for enduring this long separation.

To my brothers and sisters and their families for their support.

To my friends in Brazil João, Tulio, Kennedy, Felipe, Esmenio, Lediane, Lais Angela, Camila and Jessica for sharing this life experience with me.

To special thanks to Guilherme for all his knowledge, support and help in this investigation, because without it this would not be possible.

To the automotive fuel laboratory (LACAUT) and to all its team for facilitating the development of the present investigation.

To Lediane for his valuable help and friendship.

To all members of CAPA UFPR, especially Luciana and Bryan

Not correcting our failures is the same as making new mistakes. Confucius.

RESUMO

O estudo dos poluentes atmosféricos está se tornando cada vez mais necessário, considerando os impactos que eles geram. Entre esses poluentes, destacam-se os Compostos Orgânicos Voláteis (COV), especialmente pelo papel que esses compostos desempenham na química da atmosfera e nos efeitos nas populações expostas. Dentre os COVs, destacam-se os chamados BTEX (Benzeno, Tolueno, Etilbenzeno e Xilenos), pois esses compostos participam de reações fotoquímicas e são as principais fontes de radicais que podem oxidar NO a NO_2; sendo este último um dos principais precursores do ozônio. Os BTEX são encontrados, por exemplo, em petróleo e derivados de petróleo, como gasolina e diesel. No entanto, a principal razão para o estudo dos BTEX é por causa de seus efeitos sobre a saúde humana. Por exemplo, o Benzeno, um dos COVs altamente tóxicos, está associado a efeitos adversos à saúde, uma vez que é um carcinogênico genotóxico, o que torna necessário realizar avaliações periódicas dos BTEX. Existem diferentes metodologias para amostragem e análise de BTEX. As amostragens podem ser ativas e passivas, enquanto a dessorção da amostra pode ocorrer com o uso de solventes ou por dessorção térmica. O uso de solventes para extração começou a ser eliminado considerando seu nivel de toxicidade. Como o sistema de Termodessorção foi implementado em nosso laboratório pela primeira vez, foi necessário realizar um processo de validação da técnica analítica. A validação da técnica implica estabelecer que os instrumentos são qualificados e calibrados de acordo com seu uso neste estudo. O objetivo deste trabalho foi, portanto, validar a metodologia para a avaliação da dessorção térmica de benzeno, tolueno, etilbenzeno, m, p-xileno (BTEX) por Cromatografia Gasosa (GC) acoplada a detector de massa (MS). Para este fim, foi implementado o uso do sistema de dessorção térmica Turbomatriz ATD 300 Perkin Elmer e a análise foi feita por cromatógrafo gasoso (GC-MS) Clarus 680 Perkin Elmer acoplado a detector de massa. O processo de validação foi baseado no método de determinação COVs do EPA TO-15. O processo de otimização de um método analítico envolve a determinação de: Linearidade, Faixa de trabalho, Sensibilidade, Limite de detecção (LOD), Limite de quantificação (LOQ), Exatidão, Precisão e Robustez. A determinação da linearidade, a faixa de trabalho e a sensibilidade envolvem, especificamente a construção de curvas de calibração, as quais foram obtidas pela injeção de soluções de metanol dos compostos-alvo em cartuchos vazios pré-condicionados, limpos com o condicionador de tubo. O procedimento consistia em injetar lentamente 1 μl de soluções padrão em cada solução de calibração sob um fluxo de nitrogênio de 50 ml·min^{-1} e permitiu que o sistema purgasse por 2 minutos. Foi preparado um conjunto completo de soluções de calibração de 2 a 70 μg·ml^{-1} para a curva de calibração na faixa de massa de 0 a 80 ng. Um segundo conjunto de solucões de calibração de 90 a 300 μg·ml^{-1} foi preparado para a uma faixa de

massa de 80 a 400 ng. A preparação dos padrões foi testada usando o injetor de GC para gerar um fluxo constante de gás e a injeção foi feita com um amostrador automático, o que aumentou a repetibilidade da análise. Verificamos que cada curva de calibração mostrou coeficientes de correlação linear maiores que 0,99. O composto que apresentou maior sensibilidade foi o etilbenzeno nas duas faixas de trabalho. A sensibilidade obtida no presente estudo foi superior à obtida em estudos semelhantes para dessorção térmica. O LOD e o LOQ obtidos foram maiores que 0,5 e 1,9 μg·ml^{-1} respectivamente, para todos os BTEX analisados. Em relação à precisão do método, o tolueno apresento a melhor precisão tanto para a curva de 0 a 80 ng quanto para a curva de 80 a 400 ng. Portanto, considerando que a metodologia implementada é robusta, é possível realizar estudos que incluam amostragem passiva em diferentes áreas para a determinação de BTEX.

Palavras-chaves: Amostrador passivo, Técnica analítica de validação, Técnica de dessorção térmica, BTEX atmosférico, GC-MS.

ABSTRACT

The study of air pollutants is becoming increasingly necessary, considering the impacts they generate. Among these pollutants, the Volatile Organic Compounds (VOC) stand out, especially for the role that these compounds play in the chemistry of the atmosphere and the effects on exposed populations. Among the VOCs, the so-called BTEX (Benzene, Toluene, Etilbenzene and Xylenes) stand out because these compounds participate in photochemical reactions and are the main sources of radicals that can oxidize NO to NO_2, which is one of the main precursors of ozone. BTEX for example, are found in petroleum and petroleum products such as gasoline and diesel. The main reason for the study of BTEX is because of its effects on the health of humans. Benzene, for instance, it is one of the highly toxic VOCs, and it is directly associated with adverse health effects, since it is a genotoxic carcinogen, which makes it necessary to perform periodic evaluations of BTEX. There are different methodologies for sampling and analyzing BTEX. The samplings can be active and passive, while the desorption of the sample can occur with the use of solvents or by thermal desorption. The use of solvents for extraction has begun to be eliminated considering their toxicity. The Thermodesorption system was implemented in our laboratory for the first time and, since then it was necessary to carry out a process of validation of the analytical technique. The validation of the technique implies establishing that the instruments are qualified and calibrated for the proposed purpose. The goal our study is, therefore, to validate the methodology for the evaluation of the thermal desorption of Benzene, Toluene, Ethylbenzene o, m, p-Xylene (BTEX) by Gas Chromatography (GC) coupled with mass detector (MS). For this purpose we used the Turbomatriz ATD 300 Perkin Elmer thermal desorption system and for the analysis, we used a gas chromatograph mass (GC-MS) Clarus 680 Perkin Elmer will. The validation process was based on the method of determination of volatile organic compounds (VOCs) of the EPA TO-15. The process of optimization of an analytical method involves the determination of: Linearity, Range of work, Sensitivity, Limit of detection (LOD), Limit of Quantification (LOQ), Accuracy, Precision and Robustness. The determination of the linearity, the range of work and the sensitivity involve, specifically the construction of calibration curves. These curves were obtained by injecting methanol solutions of the target compounds into preconditioned empty cartridges, cleaned with the tube conditioner. We slowly injected 1 μl of the standards solutions in each calibration solution under a nitrogen flow of 50 ml·min^{-1} and the system was allowed to purge for 2 minutes. Subsequent dilutions were prepared to complete the set of calibration solutions from 2 to 70 μg·ml^1 and a mass range from 0 to 80 ng. A second calibration curve was made from 90 to 300 µg·ml^1 with a mass range from 80 to 400 ng. The preparation of the standards was tested using the GC injector to generate a constant flow of gas. The injection was made with an automatic sampler,

which increased the repeatability of the analysis. We verified that each calibration curve had linear correlation coefficients greater than 0.99. The compound that presented the highest sensitivity was ethylbenzene for the ranges from 0 to 80 ng and 80 to 400 ng. The sensitivity obtained in the present study was higher than that obtained in similar studies for thermal desorption. The LOD and the LOQ obtained were greater than 0.5 and 1.9 μg·ml^{-1}, respectively, for all the BTEX analyzed. Regarding the accuracy of the method, toluene was outstanding for both the curve from 0 to 80 ng and for the curve from 80 to 400 ng. Therefore, considering that the methodology implemented is robust, it is possible to carry out studies that include passive sampling in different areas for the determination of BTEX.

Key-words: Passive sampler, Validation analytical technique, Thermal desorption technique, Atmospheric BTEX, GC-MS.

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND OF ACRONYMS

ABNT Associação Brasileira de Normas Técnicas

ANSI The American National Standards Institute

APHA American Public Health Association

APIS UK Air Pollution Information System

ASTM American Society of Testing Materials

AWWA American Water Works Association

CONAMA Conselho Nacional do Meio Ambiente do Brasil

CRM Certified Reference Materials

EC-OC Elemental carbon - Organic carbon

EEA European environmental agency

FAHP fuzzy analytic hierarchy process

GHG Greenhouse Gas

IARC International Agency for Research on Cancer

ICH International Conference for Harmonization

IEA International Energy Agency

IMO International Maritime Organization

Inmetro According to the National Institute of Metrology, Quality and Technology

LGC Laboratory of the government chemist United Kingdom

LOD Limit of Detection

LOQ limit of quantification

NCR National Research Council

NIST National Institute of Standards and Technology

OCDE Organisation for Economic Co-operation and Development

PM Particulate matter

PPC programmable pneumatic control

PSCF Potential Source Contribution Function

RSD relative standard deviation

SIM Single Ion Monitoring

UFPR Universidade Federal do Paraná

UNCTAD United Nations Conference on Trade and Development

US EPA United States Environmental Protection Agency

WEF The World Economic Forum

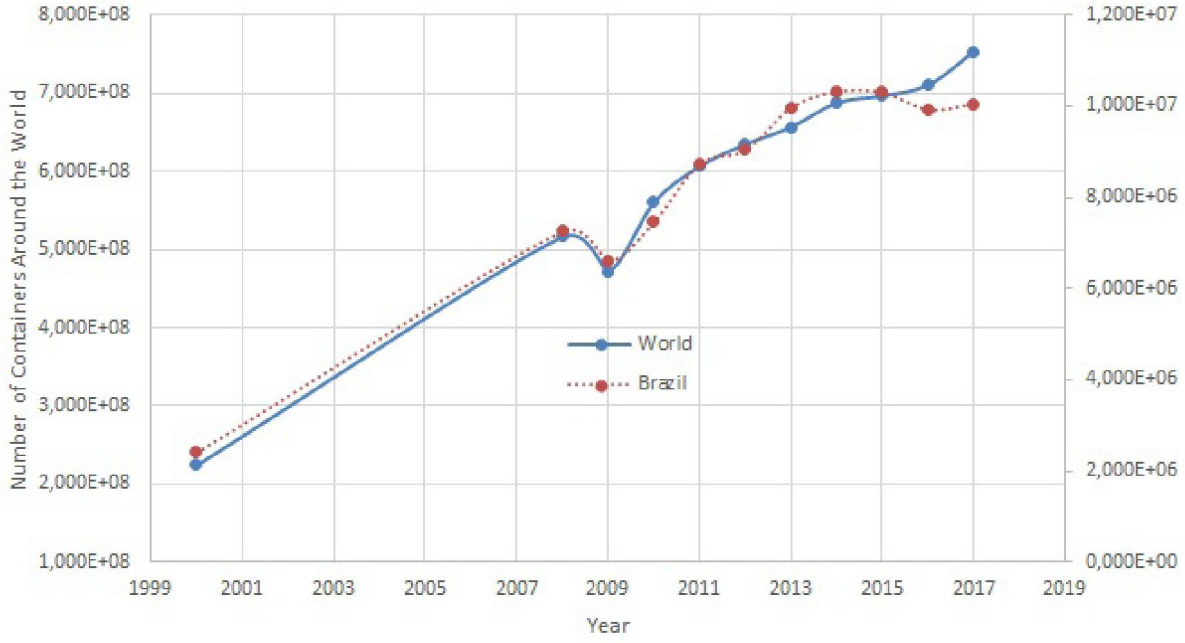
quasi-UFP quasi-ultrafine particles

CONTENTS

1 INTRODUCTION

The global container traffic is used as an indicator of cargo movement ships around the world. World Bank statistics, published in 2017, shows that the movement in the number of containers around the world varied from 225 million in 2000 to 700 million in 2016 (FIGURE 1). In Brazil, the Container port traffic (TEU: 20 foot equivalent units) movement went from 2.5 million containers to 9.3 million containers during the same period, which represents an increase of 500%. This number is much lower than China´s cargo movement that dispatched and received 41 million containers in 2000 and more than 191 million in 2017. (UNCTAD, 2017)

FIGURE 1 – The Container Traffic in Ports Worldwide



SOURCE: UNCTAD (2017)

Substances emitted from ships in port areas are scattered in the atmosphere and, in many cases, are carried to nearby urban areas, which affects air quality and endangers the health and life quality of the neighborhood. Air pollution from ship emissions are mainly sulfur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matter (PM) and organic vapors (VOCs), among others (STATISTICS, 2017). Kotrikla, Lilas and Nikitakos (2017) assessed the pollutants emissions from 40 passenger ships, cargo carriers and oil tankers in the port of Mytilen, Greece. The authors reported 441 kg of particulate matter that are less than 10μm (PM_{10}) and 282 metric tons of CO_2 from ships emissions. In-berth ships are also responsible for air pollution in port areas, mainly due to the use of motors for the supply of auxiliary devices (ADAMO et al., 2014).

The VOCs that are of specific interest for indoor and outdoor air qualities are Benzene, Toluene, Ethyl-benzene and the Xylene isomers, all of them known as BTEX (GODOI et al., 2010). Once the BTEX are present in the air, they can cause health risks when the individual is exposed for an extended period. This is especially evident with compounds such as Benzene, which is easily assimilated by the human body, even at low concentrations. Benzene in particular, is carcinogenic to humans and is probably responsible for innumerable cases of leukemia in the world (BUCZYNSKA et al., 2009).

The sampling and analytical methods for this assessment are a current challenge because of the required methodology. The conventional methods for organic compound quantification based on the active sampling of pollutants using individual pumps are relatively difficult to perform in the field due to energy availability. Then, in most cases, a solvent extraction method followed by chromatographic analysis is performed. This process shows an excellent efficiency, repeatability and compatibility with most of the adsorbents, mainly with activated charcoal, which is widely used in the occupational health-field because of its low cost and broad compatibility with organics. On the other hand, the toxicity of the commonly used solvents (dichloromethane, carbon disulfide, etc.) represents safety and sanitary health risks which implies important precautions for the operators, and an environmental problem requiring constraining and expensive recycling processes.

In passive sampling, the analytes flow easily through the collecting adsorbent, following the Fick's law (GÓRECKI; NAMIEŚNIK, 2002). The main sampling process occurs from the concentration gradient between two regions (sample and collecting spaces). Therefore, the equipment used for sampling is not complicated as in active sampling as it can increase the sampling area and no electricity is required. Furthermore, passive sampling can provide results as accurate as active sampling (ZABIEGAŁA et al., 2002) while it provides much more advantages such as the following: it is a simple and low-cost and straightforward technique; it can be applied for a high-risk area and several samples can be collected at the same time. Thus, passive sampling becomes more attractive and acceptable (ZABIEGAŁA et al., 2002).

The evaluation and determination of BTEX concentrations, both in air quality and in internal environments, is of great importance for many reasons: the significant number of sources of BTEX; the proven health effects they generate; the need to improve measurement analytical techniques, in terms of replacing toxic reagents that many of these techniques employ; and the need to improve the sensitivity and limits of detection of these analytical techniques. All this makes the determination of BTEX a latent need and one that is increasingly valid in Latin American countries such as Brazil.

2 OBJECTIVES

2.1 MAIN OBJECTIVE

Validate the methodology for the evaluation of the thermal desorption of Benzene, Toluene, Ethylbenzene o, m, p-Xylene (BTEX) by Gas Chromatography (GC) coupled with mass detector (MS).

2.2 SPECIFIC OBJECTIVES

- Optimization of the analytical method through determination of the number and range of effects that operate during the conventional use of the method EPA TO - 15.
- Optimization of the injection system of stock in absorbent cartridges (spiking) through automatic injectors of gas chromatograph MS.
- Optimization of temperatures, times, flows, pressures and configurations of the Thermodesorption system.
- Establishment of separation conditions, entrainment gas flow, furnace times and temperatures in the gas chromatograph.
- Optimization of source energy, temperatures, flows, pressures and configurations of the mass detector.

3 LITERATURE REVIEW

3.1 AIR QUALITY

Around the world there is an urgent need to install air quality surveillance systems in the main cities. These surveillance systems allow to obtain scientific bases (data on concentration of pollutants, dispersion models, etc.) they allow the development of strategies and policies to improve air quality, however, no matter how well designed the network is, like any statistical sampling system, it only represents a partial image of the behavior of the variables of contamination.

This partial image, precisely, is what makes data reported by the air quality monitoring networks not represent properly the level of exposure of the population, mainly because of the enormous variability, both in the concentrations of pollutants, and in the the same population, in terms of its location.

In addition, there is a high operating cost for the air quality monitoring networks and a limited range of pollutants monitored, for example, that contaminants such as BTEX are not monitored in most networks, despite of the demonstrated health effects related these pollutants.

Estimates of health effects on a population basis are usually calculated in relation to the excess of adverse health effects (such as increases in hospital admissions or mortality) caused by exposure to a certain level of air pollution. This involves combining information about the response to certain concentrations drawn from epidemiological or toxicological studies with the number of people exposed to each concentration of air pollution in the community being evaluated. Therefore, information on the relationship between exposure and response is necessary to estimate potential health risks.

3.1.1 Main pollutants

The Environmental Protection Agency (US EPA) (EPA, 2017) defines Air pollution as the presence or action of pollutants, under conditions such as duration, concentration or intensity, which affects human, animal or plant life and health as well as the material goods of man or community or it interfere with their welfare. The main air pollutants are toxic gases and aerosols (WHO et al., 2005); under this classification, several air pollutants can be mentioned, although those that are usually studied to assess air quality are:

- Suspend particles.
- Gases:

1. Sulfur dioxide (SO_2).
2. Nitrogen dioxide (NO_2)
3. Ozone (O_3)
4. Carbon Monoxide (CO)
5. Carbon dioxide (CO_2)
6. Volatile Organic Compounds (VOC)

Particulate matter (PM) is one of the most studied air pollutants in the world, is defined as the set of solid and / or liquid and / or gaseous particles present in suspension in the atmosphere, which comes from a variety of natural or anthropogenic sources and have a wide range of morphological, physical, chemical, and thermodynamic properties.

The main gaseous pollutants are described below:

- Carbon monoxide.
- Sulfides and nitrogen oxide.
- Volatile organic compounds (VOCs).

Although the sources of pollution are of natural and anthropogenic origin, the main sources of air pollution are the emissions derived from the activities of transport, extractive industry, agricultural and domestic heat generation (EPA, 2018a). Specifically, industrial sectors like thermoelectric plants, the petrochemical and chemical, the metallurgical in general, the food, paper and cement are undoubtedly the ones that give rise to the main effects at the environmental level as well as in the health of the exposed populations.

3.1.1.1 Particulate Matter (PM)

PM is a complex mixture of extremely small particles and liquid droplets that get into the air. Once inhaled, these particles can affect the heart and lungs and cause serious health effects. The United States Environmental Protection Agency (EPA)(1995) defines a PM as the mixture of solid particles and liquid droplets found in the air. Some particles, such as dust, dirt, soot, or smoke, are large or dark enough to be seen with the naked eye. Others are so small they can only be detected using an electron microscope. The European environmental agency (EEA) European (2018) establishes that particle pollution includes:

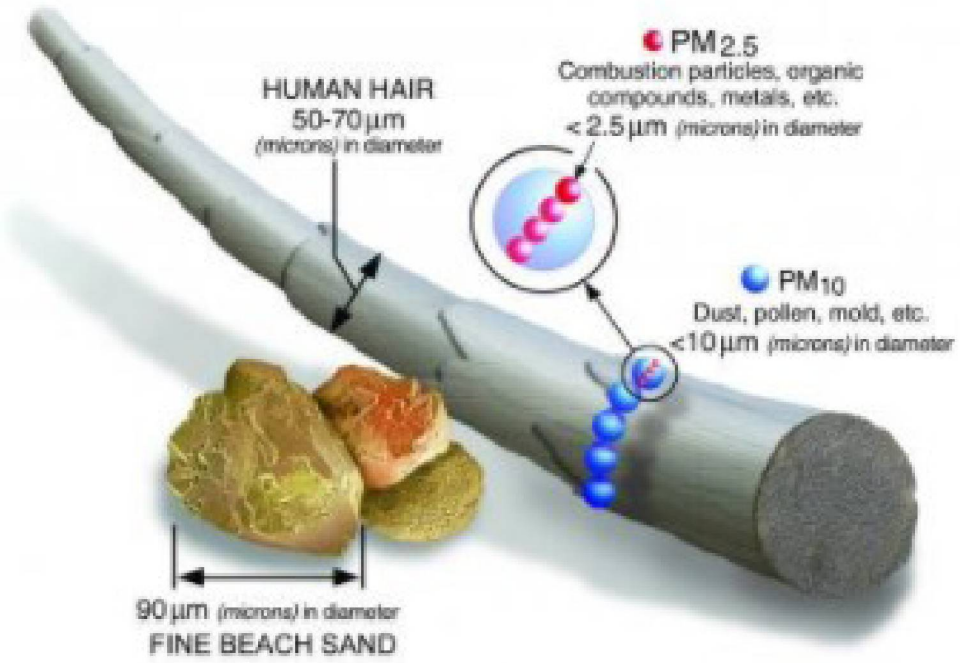
- PM_{10}: inhalable particles, with diameters that are generally equal to or less than 10 micrometers; and

- $PM_{2,5}$: fine inhalable particles, with diameters that are generally equal to or less than 2.5 micrometers.

The FIGURE 2 shows how the average human hair is about 70 micrometers in diameter – making it 30 times larger than the largest fine particle. The study of the aerodynamic properties of the particles is fundamental because it allows establishing:

- How they are transported in the air and how they can be removed from it.
- How they are absorbed in the respiratory system pathways.
- What is its chemical composition, and what is the source of the particles?.

FIGURE 2 – Comparison PM size and a hair



SOURCE: http://www.epa.gov/pm-pollution/particulate-matter-pm-basicsPM

The particulate matter does not have a defined form, so, in order to study it, it is necessary to assume that each particle corresponds to a sphere, which will facilitate the interpretation of its aerodynamic behavior. Therefore, the characterization of the particulate material is a function of this aerodynamic size, which is generally known simply as "particle size". At present, not only the aerodynamic diameter is being studied, but also the number of particles is measured. This parameter is useful in terms of the fact that, depending on the sources, the number of particles of smaller aerodynamic size can be significantly higher, which potentials their health effects.

WHO et al. (2003) in the report on Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide divides the particulate material into two groups:

- The coarse fraction contains the larger particles with a size ranging from 2.5 to 10 μm (PM_{10} - $PM_{2.5}$).
- The fine fraction contains the smaller ones with a size up to 2.5 μm ($PM_{2.5}$). The particles in the fine fraction, which are smaller than 0.1 μm, are called ultrafine particles.

WHO et al. (2003) establishes that most of the total mass of airborne particulate matter is usually made up of fine particles ranging from 0.1 to 2.5μm. The importance of ultrafine particles lies in that, although they often contribute a small percentage to the total mass, they are the most numerous, since they represent more than 90 % of the number of particles.

3.1.1.2 Gaseous Pollutants

Earth's atmosphere is a dynamic system of natural gases that are necessary to sustain life. In that area, high levels of specific gaseous pollutants can cause ozone depletion and other problems for living organisms. One of the main sources of gaseous air pollutants is fuel combustion in stationary sources, such as coal-burning power plants, as well as emissions from automobiles. While these gases are not the only ones contributing to air pollution, they are regarded as dominant sources of this worldwide problem. The gases considered as the most significant polluters or of more considerable attention are presented below:

- CARBON OXIDES: are among the most well-known greenhouse gas that contributes to the air pollution plaguing the Earth's atmosphere. Carbon monoxide (CO) is a poisonous gas, dangerous due to its lack of odor and color that's released into the atmosphere with the incomplete combustion of fuels, such as coal, wood or other natural sources, as well as exhaust from automobiles. Carbon dioxide (CO_2) is the greenhouse gas widely considered the main air pollutant in the Earth's atmosphere. CO_2 is essential to support living organisms, and it is considered a dangerous air pollutant caused by human activities such as deforestation and the burning of fossil fuels. It is responsible for more than half of the global warming trend, carbon dioxide restricts infrared radiation leaving the Earth's surface, causing the "greenhouse effect." (CLIMATE CHANGE, 2006).
- NITROGEN OXIDES (NOx): WHO et al. (2005) establishes in the Air quality guidelines for air quality that Animal and human experimental studies indicate that NO_2 is a toxic gas with significant health effects (concentration > 200 $\mu g \cdot m^{-3}$). It also defines them as a marker of combustion related pollutants, in particular, those emitted by road traffic or indoor combustion sources. WHO also establishes

that NO_2 in the presence of hydrocarbons and ultraviolet light is the main source of tropospheric ozone and nitrate aerosols.

- SULFUR OXIDES (SOx): EPA (2017) establishes that the main sources of generation of SO_2 are the burning of fossil fuels that contain sulfur as contaminants and energy generating plants. However, there are other sources of SO_2 generation such as the extractive industry of metals, locomotives, ships and any type of vehicle or engine that uses fuels with sulfur content. In addition, SO_2 is originated equally from natural sources such as volcanoes.

  EPA (2017) establishes that among the impacts generated by SO_2, the formation of acid rain stands out, besides the generation of very dangerous air pollutants, which have effects on plants and animals and as generate cause different respiratory problems, especially in children and the elderly.

- OZONE (O_3): WHO et al. (2003) consider ozone as the most important photochemical oxidant in the troposphere. Ozone is formed by the chemical reaction in the atmosphere of nitrogen oxides and volatile organic compounds, all in the presence of sunlight, which is why their concentrations are higher at midday and in urban regions with high vehicular activity. These are the regions that produce the largest and most significant emissions of both VOCs and NOx. WHO et al. (2003) also establishe in then report on health aspects of pollutants that the ozone causes adverse health effects, both chronic and acute effects. However, WHO concludes that more and better epidemiological studies are needed to establish the health impacts of ozone more clearly.

3.1.2 Volatile organic compounds (VOC)

The Environmental Protection Agency (EPA) defines the Volatile Organic Compounds (VOC) as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity"(EPA, 2017).

VOCs are compounds that evaporate under normal conditions of pressure and temperature (OU et al., 2016). The volatility of these compounds is higher within lower boiling point temperature. Taking this characteristic into account (WHO et al., 1989) classify VOCs according to what is illustrated in TABLE 1.

Different air quality management tools have been implemented in different regions around the planet. In all of them the limit value of a specific pollutant concentration in the atmosphere is determined associated with an exposure time interval, so that the environment and the health of the population are preserved, in relation to the risk of

TABLE 1 – Classification of inorganic - organic pollutants (Adapted from World Health Organization (WHO))

Description	**Abbreviation**	**Boiling Point Range (℃)**	**Example Compounds**
Very Volatile (gaseous) Organic Compounds	VVOC	<0 to 50-100	Propane, butane, methyl chloride
Volatile Organic Compounds	VOC	50-100 to 240-260	Formaldehyde, d-limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal
Semi Volatile Organic Compounds	SVOC	240-260 to 380-400	Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB))

damage by inhalation of this air. In Brazil, this tool corresponds to resolution of Conselho Nacional do Meio Ambiente - CONAMA/Brazil 491 of November 2018 (BRASIL, 2019), which establishes the permissible limits for criteria pollutants. However, in this resolution there are not permissible limits for any of called VOCs.

In the United States and Europe, VOCs are regulated only because of their active participation in the generation of ozone. However, only a few VOCs are reactive. Accordingly, EPA (2017) considers that a high percentage of volatile organic compounds are non-reactive or have a negligible reactivity to form ozone, so under these conditions they are exempt from the definition of VOC used by the EPA in its' regulation.

3.1.2.1 VOC's Sources

EPA (2018b) considers the following types of VOC sources categories for the calculation of VOC emission indicators:

1. Fuel combustion, which includes emissions from coal, gas, and oil-fired power plants and industrial, commercial, and institutional sources, as well as residential heaters and boilers.
2. Other industrial processes, which includes chemical production, petroleum refining, metals production, and processes other than fuel combustion.
3. On-road vehicles, which includes cars, trucks, buses, and motorcycles; and
4. Non-road vehicles and engines, such as farm and construction equipment, lawnmowers, chainsaws, boats, ships, snowmobiles, and aircraft.

5. Biogenic VOC emissions (excludes VOC estimates of prescribed burning and other miscellaneous sources)

3.1.2.2 Formation Process

EPA (2018b) considers that volatile organic compounds originate through evaporation processes, both anthropogenic sources and natural sources, as well as the emission of fossil fuels. These compounds, due to their volatile nature, are extremely unstable and, therefore, have to remain as gases, while less volatile VOCs tend to remain in the solids or liquids that contain them or on surfaces.

3.1.2.3 Reactions in the atmosphere

Seinfeld and Pandis (2016) state that VOCs vary from very reactive to almost inert in the atmosphere. Some of the biogenic compounds (terpenes and isoprene) are oxidized in a few hours, while others have lifetimes with considerable periods. Atkinson (2007) establishes that the main atmospheric sink for aromatic compounds is the reaction with the hydroxyl radical. The mechanisms by which the reaction of the VOC with the hydroxyl radical occurs are still under investigation. However, the main reaction of the VOCs is the elimination by oxidation promoted by the hydroxyl radical (OH), which is produced by the action of the UV rays contained in sunlight onto the ozone. UK Air Pollution Information System (APIS) found that "the more complex VOC oxidation leads to fragmentation (Radicals), the production of a range of reactive free radicals and more stable smaller molecules, such as aldehydes. These in turn are oxidized or photolyzed to the possible products of carbon dioxide and water." At night, when OH radicals are not present in significant quantities, other radical reactions play an important role (APIS, 2018).

Seinfeld and Pandis (2016) also found that there's a wide range of VOC reaction rates, which means that the range of transport distances is also large, extending from around 100 km to the entire troposphere. For this reason, the National Research Council (NCR) established this known mechanism of reaction VOCs with hydroxyl groups, occurs both at urban and regional level (NRC et al., 1992). It's also important to mention that unlike many inorganic contaminants, it seems that the absorption and elimination of VOCs by vegetation is quite slow and has little impact on the processes of elimination in general.

3.1.2.4 Health Effects by VOCs

Volatile organic compounds (VOCs) are commonly found in the environment, workplace and consumer products (EZQUERRO et al., 2004; SCHNEIDER et al., 2001; ZABIEGAŁA et al., 2002). Therefore, Human are easily exposed to these chemicals

through the skin, breathing and eating, and even at low concentration these chemicals present a long-term health risk (SHOJANIA et al., 1999). There is some evidence on studies conducted on animals which indicate that some of these VOCs have carcinogenic or mutagenic effects on tissue development. Benzene is one of these chemicals, which is classified by International Agency for Research on Cancer (IARC - WHO) as a human carcinogenic compound group A (RESEARCH ON CANCER; IARC, 2017). Moreover, Benzene, Toluene, and Xylene, known as BTX, are the markers for human exposure to VOCs; consequently, the monitoring of these three compounds is necessary to evaluate the risk to human health (BEGEROW et al., 1996).

3.1.2.5 Effects on surrounding populations

The effects on the population surrounding the points of generation of VOCs in general and BTEX in particular are diverse and innumerable. Below is a small sample of the different effects of the VOCs reported in the literature.

Studies conducted by Broday et al. (2006) and Zalel, Broday, et al. (2008) in the Bay of Bay Israel showed that ozone concentrations are regulated by NOx and VOCs, and that these, in turn, are related to vehicular traffic, and that VOCs are the limiting source for the generation of ozone. Similarly, it was found that service stations are a source of significant generation of BTEX.

On the other hand, studies conducted by Delfino et al. (2003a) about adolescents of Los Angeles, who live in areas of high vehicular traffic, showed a positive association between the symptoms related to asthma and the criteria pollutants (O_3, NO_2, SO_2 and PM_{10}), as well as with Elemental carbon - Organic carbon (EC-OC), VOCs (BTEX, Formaldehyde, Acetaldehyde, Acetone, 1,3 Butaldehyde and Tetrachlor Ethylene).

While Singla et al. (2012) found that high vehicular traffic routes and fuel service stations in Agra (India) generated in two strains of Salmonella mutagenic response statistically significant by the presence of the BTX mutagenic agents, similar results were found by Rekhadevi in stations of Andrha Pradesh service (India), as this study showed that exposure to BTX has the potential to cause genetic changes in exposed subjects.

Egeghy, Tornero-Velez and Rappaport (2000a) also found that the personnel that provides the fuel supply (users and workers) present a high level of exposure to Benzene, and that it is statistically significant, due to the high concentrations of Benzene found in the North Caroline stations (US) Additional results of the effects of Benzene were reported by Gioda et al. (2005) in Volta Redonda Brazil, who found that high levels of Benzene concentration are statistically correlated with the rates of cancer in the city.

3.1.2.6 Occupational effects

Different investigations around the world show the repercussions of exposure to BTEX in health. Delfino et al. (2003b) reported low, but significant Spearman correlation coefficients for benzene in end-exhaled air vs. benzene in the ambient air based on a fixed-site measurement (not personal air sampling, r=0.30) and for benzene in end-exhaled air vs. o-xylene and m/p-xylene in ambient air (r=0.28 and 0.33). Much stronger correlations between personal exposure and breath concentration were observed for benzene during self-service refueling (EGEGHY; TORNERO-VELEZ; RAPPAPORT, 2000b), for Toluene in shoe manufacturing workers (PERIAGO; PRADO, 2005) and in workers of an unspecified chemical factory (GHITTORI et al., 2004). Most of these studies dealt with relatively high occupational exposures. In studies with much lower benzene exposure levels, such correlations were much weaker (PERBELLINI et al., 1988), or not observed (MONEY; GRAY, 1989). The most important factor would be the difference in the time frame: diffusive samplers are for monitoring exposures over a designated and, fixed period, therefore, they may be adequate to represent exposure over extended periods, especially in occupational environments.

3.1.2.7 BTEX

The main source of VOCs in urban areas is road traffic and other combustion processes, and fuel evaporation. BTEX (benzene, toluene, ethylbenzene and m,p,o xylene) are mainly released from traffic vehicles. For example, YOU et al. (2007) and Fernandes et al. (2002) noticed that the most abundant VOC in some urban atmospheres was toluene, followed by m,p-xylene, and benzene, although high concentrations of 1,4-dichlorobenzene were also found by Fernandes et al. (2002) Industrial areas, particularly oil refineries and the chemical industry, are also essential sources of VOCs, which are produced mainly in the production processes, the storage tanks, the transport and the waste areas. Therefore, bellow we present what the BTEX are.

Aiming to understand the implications of the presence of BTEX in the air, TABLE 2 show the definitions for the BTEX accordind to the European environmental agency (EUROPEAN, 2018). TABLE 2 shows some of the properties of the BTEX, such as the recurrent presence of this type of compounds in industrial applications, and how it is significant in fuels of massive use, it also highlights its enormous reactivity, wich results in a more significant influence on the potential impacts and effects on health (APIS, 2018).

3.1.2.8 Ratios between BTEX

Ratios of individual compounds are frequently used to obtain preliminary information on their emission characteristics and the extent to which they participate in

TABLE 2 – Properties of BTEX

Properties	Benzene	Toluene	Ethylbenzene	m, p, o Xylene
Color	Colorless	Colorless	Colorless	Colorfull
Types of Sources	Antropogenic Natural process	Antropogenic Natural process	Antropogenic Natural process	Antropogenic Natural process
Principal Sources	Industry	Making gasoline and other Fuels	Making gasoline and other Fuels	Industry
Secundary sources	Burning Coal and oil Storage operations	Paints, Paints thiners Finger nail polish Adhesives, rubber	Inks, insecticides, paints, pesticides carpet glues, varnish and paint	Chemical industries petroleum, coal tar formed during forest fires.
Reactions	Other chemicals and breaks down a few days		breaks down by reacting with other chemicals found naturaly in water	breathing it in contamined air
Build	Does not build up in plants or animals	Not concentrate or build up to high levels in animals or humans	People are exposed to ethylbenzene at work	

Source: EEA, 2018

chemical reactions (AN, 2005; GARZÓN et al., 2015). The ratio of Toluene to Benzene (T/B) is used to explore the relative abundance for traffic and non-traffic sources. Depending on gasoline composition T/B from 2 to 3 indicates traffic as a primary source of pollution, while values less than 0.5 correspond predominantly to industrial sources. Therefore, environmental Toluene/Benzene (T/B) ratios that are significantly smaller than vehicle emission rates are expected to travel and degrade, while higher T/B ratios may reflect relatively new sources of vehicle emissions. An (2005) and Garzón et al. (2015) proposed a specific T/B ratio of 2 to be an approximate indicator of motor vehicle emissions within the measured VOCs, while a ratio larger than 2 indicates the presence of other toluene sources.

A significant number of studies using T/B ratios have been developed around the world, in order to establish the origin of BTEX. For example, Fernandes et al. (2002) found that in different locations where the average ratio in the first evaluation (Dec/95-May/96) were: 0.4 (FEEMA), 1.1 (Belmonte), 0.3 (Retiro), 0.4 (Aeroclube) and 0.3 (Centro de Pesquisas). In the second evaluation (April-May/99) FEEMA presented a T/B ratio of 0.22 and Retiro of 0.14. These ratios suggest that, during both assessments, the organic compound pollution is mainly due to industrial emissions. This motif was used to identify the predominant sources of hydrocarbons in 43 Chinese cities (BARLETTA et al., 2002). It was observed that the environmental B/T ratio of 10 cities were more affected by vehicle emissions as the main source of hydrocarbons. Geng et al. (2007) found that T/B values in urban ambient air varied from 0.3 to 0.8 at urban sites in Shanghai.

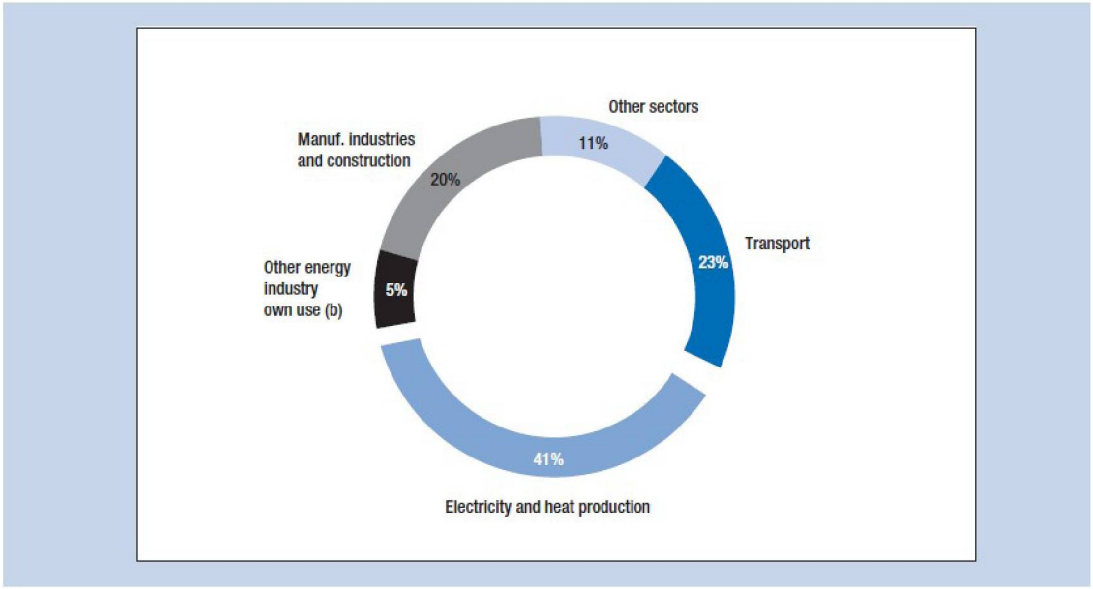
T/B ratios were further confirmed by correlations between some traffic markers (Benzene, Toluene and 1,3-butadiene) with Etine and Ethane, indicating the ability of the T/B ratio to differentiate the areas dominated by traffic emission (BUCZYNSKA et al., 2009). SWango et al. (2015) and Wangu et al. (2015) reported T/B ratios were

1.3–2.2 and 2.1–3.0 in tunnels dominated by light vehicles and heavy diesel vehicles, respectively. The relations T/B could be used in field studies to evaluate the existing emissions in the ports, in addition to proposing new relationships for the emissions generated by the ships that arrive at the port of Paranaguá.

3.1.3 Pollutant area sources (port storage)

The report of the United Nations Conference on Trade and Development (UNCTAD) affirmed that the transport sector is estimated to have accounted for around 13% of all the world Greenhouse Gas (GHG´s) in 2004 (TEAM; PACHAURI; MEYER, 2014). Logistics, including freight transport and "logistics buildings" account for 5.5% of global GHG emissions. Of this total, freight transport accounts for the lower share of 90% or 4.95% of total GHG emissions and, of this, (LAMMGÅRD, 2012) in terms of CO_2 emissions, the transport sector is estimated to have accounted for around 23% of global CO_2 emissions in 2009 (OLIVIER; PETERS; JANSSENS-MAENHOUT, 2012). Statistics published by the International Energy Agency (IEA) in 2011 show that the transport industry is the second largest CO_2 emitting sector after electricity and heat production (FIGURE 3). FIGURE 4 show calculations made by the International Maritime Organization (IMO) and compares CO_2 emissions from significant freight transport modes.

FIGURE 3 – World CO_2 emissions from fuel combustion by sector, 2009 (a)



SOURCE: IEA Statistics (2011)
NOTE: a) Includes international bunkers in the transport sector. b) Includes discharge from own use of petroleum refining, the manufacture of the solid fuels, coal mining, oil and gas extraction and other energy-producing industries.

According to the Buhaug et al. (2009), shipping was estimated to have ac-

counted for 3.3% of the global emission during 2007. International shipping was responsible for 2.7% of the worldwide CO_2 in 2007. In the absence of comprehensive policies to control emissions from international shipping, ship emissions may increase by 200-300% by the year 2050 (compared to the emissions in 2007) due to the expected continued growth in global seaborne trade (BUHAUG et al., 2009).

3.1.4 Mobile sources in ports

The International Maritime Organization (IMO) estimates that the transport sector is considered to have accounted for around 13% of all world Greenhouse Gas (GHG) in 2004 (MEEHL et al., 2007). Logistics, including freight transport and logistics buildings (Logistics and Supply Chain Industry Agenda) account for 5% of global GHG emissions. Of this total, freight transport represents charred contributions of 90% or 4.95% of total GHG emissions. In terms of CO_2 emissions, studies estimated that the transport sector accounted for around 23% of global emissions in 2009. According to IEA calculations (Fuel combustion - Edition 2011), as shown in FIGURE 3, CO_2 emissions from the transport industry sector is the second largest CO_2 emitter after the production of electricity and heat.

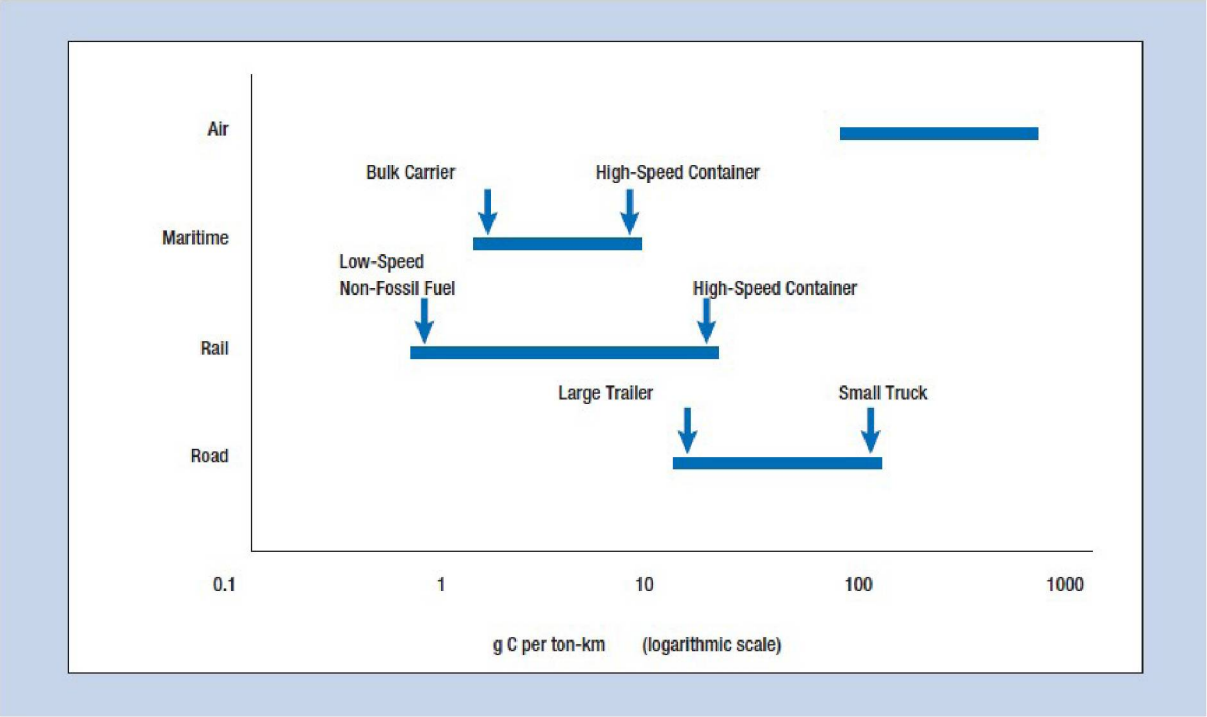
FIGURE 4 compares CO_2 from significant freight transport methods. It shows that regarding grams of CO_2 produced for every ton carried over one kilometer, air transport is the most considerable emitter, followed by road. It should also be remarked that air and road transportation are the two most expensive methods of transportation regarding freight rates per volume (CLIMATE CHANGE, 2006).

From the results published by Asariotis et al. (2011) about the growth of maritime transport, the following conclusions stand out:

- Transport-related CO_2 emissions are estimated to increase by 57% worldwide (1.7% a year) for the period 2005–2030 (Partnership on Sustainable Low Carbon Transport).
- More than 80% of the predicted growth in transport emissions would be in developing countries (with China and India alone accounting for more than 51% of the global increase and with most of the emissions being generated by land transport.
- ***Air pollution is also expected to be more intensive in developing countries due to the quality of the fuel used for propulsion and the conditions, equipment and vehicles, in particular, the aging trucks.***

A significant part of this traffic is related to the freight transportation system that moves containers with heavy-duty diesel trucks. In addition to the large commercial marine vessels that transport these goods in and out of ports, these trucks are a

FIGURE 4 – Comparison of CO_2 emissions in freight transport by mode of transport (Grams carbon per ton freight carried per kilometer)



SOURCE: Buhaug et al. (2009)

significant source of pollution in the immediate vicinity of the port. As the volume of trucking and freight movement increases, near-road air quality along transportation routes could be affected both inside and outside port boundaries (HAGLER et al., 2013). The Organisation for Economic Co-operation and Development (OCDE) reports that trucks can produce over 40% of the pollution where they only account for 10 % of all transport operations in urban areas (URBAN FREIGHT LOGISTICS, 2003).

3.1.5 Atmospheric pollutants generated in ports

Tang et al. (2017) reported that traffic is one of the significant users of energy and one of the major polluting sectors. Traffic is considered a significant cause of the monitored exceedances of limit values in ambient air quality in urban areas (C. GUERREIRO, 2013). In 2011, the contribution of road transport emissions to nitrogen oxide (NOx) and carbon monoxide (CO) in Europe amounted to 40% and 26%, respectively (C. B. GUERREIRO; FOLTESCU; DE LEEUW, 2014). Traffic is also an important source of particle emissions (PM_{10} and $PM_{2.5}$) (PANT; HARRISON, 2013).

In Tseng, Ding and K.-H. Chang (2017) developed an investigation called "Evaluating key environmental risk factors for pollution at international ports in Taiwan". The primary purpose of this paper is to use the fuzzy analytic hierarchy process (FAHP) approach to evaluate the critical environmental risk factors for pollution at international

ports in Taiwan. First, this study constructed a hierarchical structure with three aspects of risk and thirteen risk factors, and then it proposed a model of FAHP. Based on the data from the questionnaires answered by analytic hierarchy process (AHP) experts, the FAHP approach was used to determine the critical environmental risk factors. The study concludes that:

1. Air pollution is the most crucial aspect of environmental contamination at international ports in Taiwan;
2. In order of relative importance, the top five critical environmental risk factors for pollution at international ports in Taiwan are the oil leaks from ships, volatile organic compounds (VOCs), exhaust emissions from ships at berth, harmful coatings on hulls of ships, and the failure of the ships to use low-pollution fuel. Furthermore, some discussions are provided for port authority in Taiwan

Different studies around the world have presented results of the effects of the pollution generated in ports. Burwell-Naney et al. (2017) and Han et al. (2017) found that concentrations of most elements were higher in the low socioeconomic status (low-SES) community than in the high-SES community. In the quasi-ultrafine particles (quasi-UFP) size mode, the largest difference in levels of individual constituents of PM between the two communities was for low-SES, possibly because of to the proximity of the low-SES community to shipping and refinery activities near the Port of Houston. Similar findings were reported in Gregoris et al. (2016), who also did not observe a significant reduction in the contribution of ship traffic and harbor activities to particulate PAHs and metals. While Super et al. (2017) found results that verified clear emission signals from three sectors of origin, within which the main ones are related to industrial activities in the port and in residential areas. To confirm the impact of the emissions in ports, Butterfield and Quincey (2017) affirms that currently, far from the port (offshore), the use of lower quality fuels is authorized, which allows the predicting of sulfur emissions from combustion in the ships, exceeding those of all the terrestrial sources of the EU for 2020.

Bailey et al. (2004) found that Marine ports are among the most poorly regulated sources of pollution in the United States, and their goods movement activities are primarily of diesel engines that emit complex mixtures of particulate matter (PM) $PM_{2.5}$, coarse PM_{10}, volatile organic compounds, nitrogen oxides, sulfur oxides, and other ozone-depleting substances.

The California Environmental Protection Agency has already deemed 40 components of diesel exhaust as cancer-causing (EPA 2006), thereby posing a significant cancer risk to populations living near diesel emission sources. The similar danger in cancer is conceivable in Charleston (RICE et al., 2014) because the port expansion

will increase diesel truck trips by 70% per day, corresponding to the current estimate of 10.000 vehicle trips/day (SVENDSEN et al., 2014).

Dingo et al. (2017) found that the results of Potential Source Contribution Function (PSCF) showed that the pollution in July was mainly influenced by long-range transport while it was mainly associated to local and intra-regional traffic in August. Besides the contributions of anthropogenic sources from Yangtze River Delta and Pearl River Delta region, emissions from the ship from East China Sea also made a significant contribution to the high loading of $PM_{1.8}$ and $PM_{1.8}$ associated with NO_3^-, NH_4^+, and EC in July. SO_4^{-2} in Shanghai was dominantly ascribed to anthropogenic sources, and the high PSCF values for $PM_{1.8}$ associated with SO_4^{-2} observed in August was mainly due to the emissions from the ship in Shanghai port. Barkley et al. (2017) and Tichavska and Tovar (2015) found similar results.

3.2 LEGISLATION ON AIR QUALITY

TABLE 3 presents the permissible limits established by different entities for one of the most significant air pollutants. TABLE 3 show the values of the particulate matter; as can be seen, the values of the Brazilian regulations are above those of the European norm and the World Health Organization.

TABLE 3 – Permissible limits for particulate matter

Parameter	**Directive 2008/50/EC**	**WHO guide 2006**	**Resolução CONAMA n° 3/1990**
PM_{10}	40 $\mu g{\cdot}m^{-3}$ annual average	20 $\mu g{\cdot}m^{-3}$ annual average	50 $\mu g{\cdot}m^{-3}$ annual average
$PM_{2.5}$	25 $\mu g{\cdot}m^{-3}$ annual average	10 $\mu g{\cdot}m^{-3}$ annual average	—-

The directive of the European community of nations for air quality were created with three fundamental objectives: to define and establish the objectives for air quality; to evaluate air quality and collect air quality data. These objectives serve as criteria for decisions making. TABLE 4 summarizes the parameters that have permissible limits in each of the directives of the European Economic Community in recent years.

The importance of the directives of the European community is that since the year 2000, they establish permissible limits for one of the BTEX, such as Benzene. Below is a summary of the guidelines and parameters that have been legislated by the European community. Brazilian regulations do not establish permissible limits for BTEX

TABLE 4 – Directives EC

Directive	**Pollutans**								
1999/30/EC	SO_2	NO_2	NOx	PM_{10}	Pb				
2000/69/EC	Benzene	CO							
2002/03/EC	Ozone (O_3)								
2004/107/EC	PAH	Cd	As	Ni	Hg				
2008/50/EC	SO_2	NO_2	NOx	PM_{10}	$PM_{2.5}$	Pb	Benzene	CO	O_3

in air quality. The directive 2008/50/EC of June 11, 2008 (See TABLE 5) establishes the Annex XI of the limit values for human health protection.

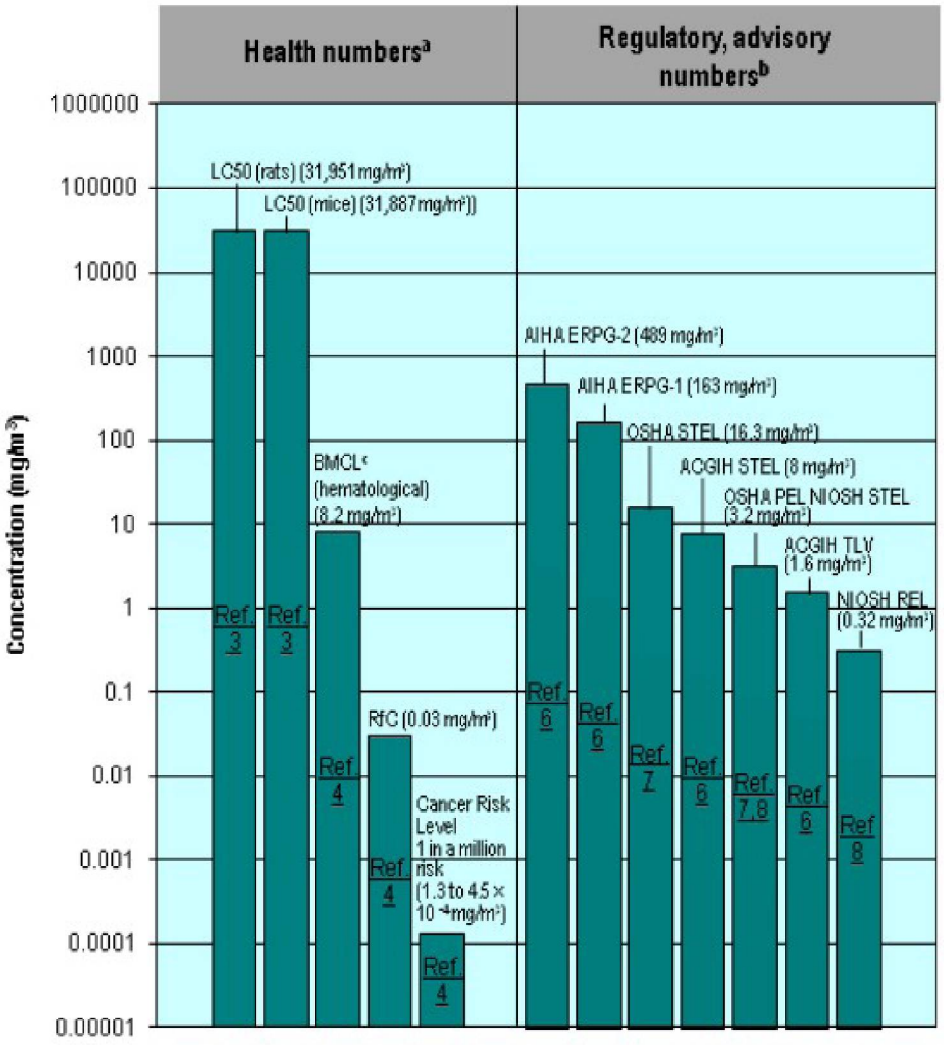
TABLE 5 – Value Limit Directive 2008/50/EC

Parameters	**Averaging Period**	**Limit Value**	**Margin Tolerance**
PM_{10}	One Day	50 μg·m^{-3}	**< 35 times a calendar year**
	Calendar Year	40 μg·m^{-3}	
Sulphur dioxide	one hour	350 μg·m^{-3}	**< 24 times a calendar year**
	One Day	125 μg·m^{-3}	**< 18 times a calendar year**
Nitrogen dioxide	one hour	200 μg·m^{-3}	**< 18 times a calendar year**
	Calendar Year	40 μg·m^{-3}	
Benzene	Calendar Year	5 μg·m^{-3}	
Carbon Monoxide	8 hou daily	10 mg·m^{-3}	
Lead	Calendar Year	0.5 μg·m^{-3}	

FIGURE 5 summarizes existing environmental and occupational health standards for Benzene, one of the most hazardous BTEX. The Environmental Protection Agency of the United States (EPA) and the World Health Organization (WHO) have different permissible limits for BTEX, however, both agree that BTEX have carcinogenic and mutagenic effects in human health, even with concentrations of a few parts per billion (ppb). For example, FIGURE 5 shows that for concentrations from 0.13 to 0.45 μg·m^{-3}, the risk of cancer begins to increase from 1 in a million inhabitants.

Benzene is a well-known human carcinogen for all routes. It has been established that long-term exposure to high concentrations of Benzene may cause circulatory, immunological and neurological dysfunctions (NA; MOON; Y. P. KIM, 2005), while other BTEX play a significant role in sick building syndromes. These considerations prompted the legislature to limit benzene concentration to 1 (0.3 ppb), 3 (1 ppb) and 5 (1.5 ppb) μg·m^{-3} in the USA, Japan, and the European Union, respectively and their values for other BTEX (CAMOU; TAMECHIKA; HORIUCHI, 2012).

FIGURE 5 – Health and regulatory values for Benzene



SOURCE: url:https://www.epa.gov/sites/production/files/2016-09/documents/benzene.pdf

3.3 VALIDATION OF ANALYTICAL TECHNIQUES

Analytical method validation is the process of demonstrating that a systematic procedure is suitable for its intended purpose. The methodology and objective of the analytical procedures should be defined and understood before initiating validation studies. This understanding is obtained from scientifically-based method development and optimization studies. According to the Guidance on validation of analytical methods (ABNT NBR ISO/IEC 17025) of 2016 (GUIDELINE, 2005) for validation data must be generated under a protocol approved by the sponsor following current good manufacturing practices with the description of the methodology of each validation characteristic and predetermined and justified acceptance criteria, using qualified instrumentation.

According to the National Institute of Metrology, Quality and Technology - Inmetro - The Brazil Guidance on validation of analytical methods (ABNT NBR ISO/IEC

17025) (2016, page 6) presents which methods are appropriate for the intended use and the standards of the parameters that shall be validated:

- Non-standard methods;
- Methods created/developed by the laboratory itself;
- Standardized methods used outside the scopes for which they were designed
- Extensions and modifications of standard techniques.

These guidelines (ABNT NBR ISO/IEC 17025) (2016) also present three processes that should be taken into account in the validation method:

1. The validation process of a method should be described in a procedure;
2. Studies shall be carried out with properly calibrated and validated equipment and instruments;
3. The operator carrying out the studies must be proficient in the research area.

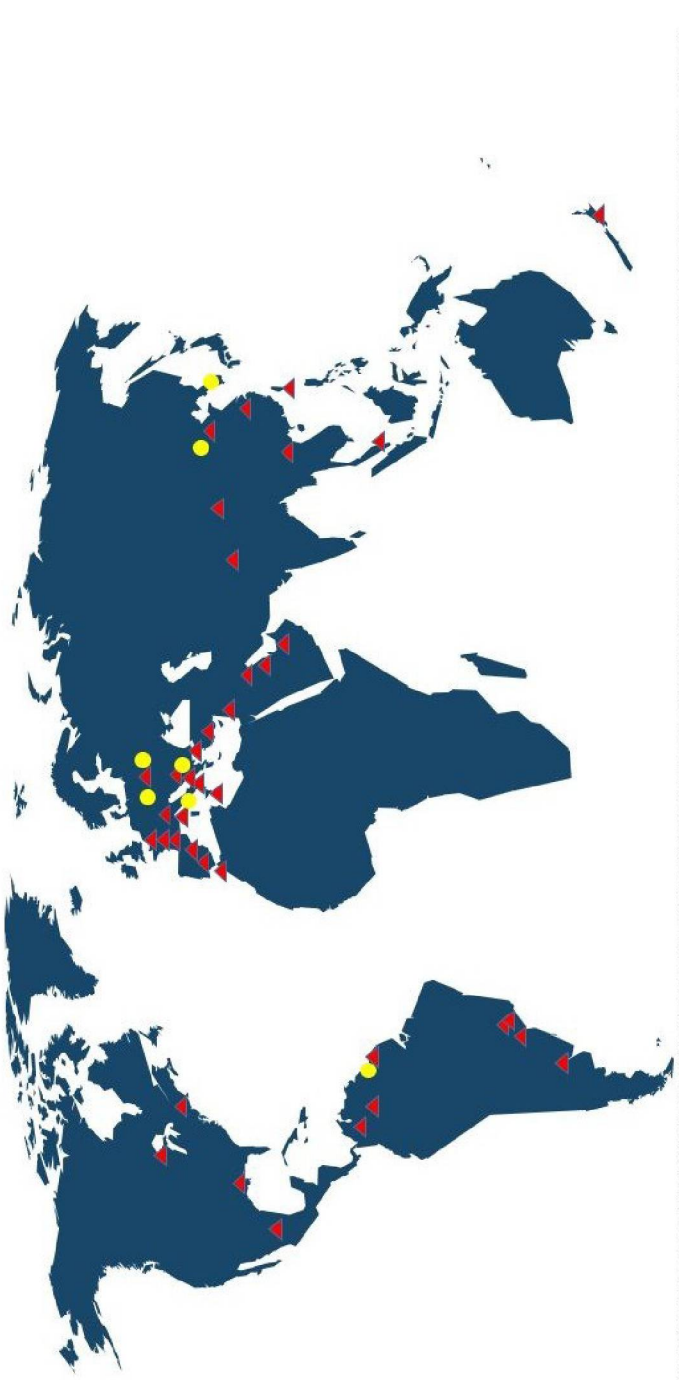
Typical validation characteristics listed in the guidelines are:

- Specificity
- Precision (repeatability, intermediate precision, and reproducibility)
- Range
- Limit of Detection
- Limit of Quantitation
- Linearity.
- Accuracy.

3.3.1 Normalized and non-normalized Methods

Normalized methods are the ones developed by a standardization organization or other organizations (e.g., ABNT, ASTM, ANSI or APHA / AWWA / WEF), whose methods are accepted by the respective technology sector. The non-standard method it is the one developed by the laboratory itself or other parts or adapted from standardized and validated methods. For example, methods published in technical journals, methods of equipment manufacturers, methods using test kits and portable instruments.

FIGURE 6 – Studies of BTEX around the world



4 (RISK, 2004), 5 (OU et al., 2016), 7 (BUTTERFIELD; QUINCEY, 2017), (8a), 9 (Maria Vittoria PRATI et al., 2015), 10 (BURWELL-NANEY et al., 2017), 13 (TICHAVSKA; TOVAR, 2015a), 14 (ADAMO et al., 2014), 15 (TSENG; J. -F. DING; K. - H. CHANG, 2017), 17 (CHATZINIKOLAOU; OIKONOMOU; VENTIKOS, 2015), 18 (GREGORIS et al., 2016), 19 (MERICO et al., 2016), 20 (SUPER et al., 2017), 21 (M. LEE et al., 2017), 22 (X. DING et al., 2017), 23 (MURENA; M. PRATI; QUARANTA, 2014), (BARKLEY et al., 2017), 25 (TOLIS et al., 2015), (TICHAVSKA; TOVAR, 2015b), 30 (Y. ZHANG et al., 2017), 31 (LÓPEZ-APARICIO; TØNNESEN; NEILSON, et al., 2017), 34 (ALVES et al., 2016), 151(DURÁN-GRADOS et al., 2018), 184 (Veronika EYRING et al., 2005), 188 (HAGLER et al., 2013).

SOURCE: Source: The author

3.3.2 EXPECTED RESULTS

BTEX compounds are of interest, especially benzene, because it is a carcinogenic compound whose European air quality reference value is set at 5 $\mu g \cdot m^3$. (European Union Directives 2000/69/EC EU. Therefore, **with relatively low concentration of BTEX we need to use particularly sensitive analytical techniques**.

The number of studies carried out for the determination of BTEX in different matrices is quite large, as well as the analytical techniques that have been developed to determine it. FIGURE 6 presents the results published in sampling or pilot studies carried out for the determination of BTEX in air quality.

Owing to the extensive number of articles, we are going to present only those studies that were performed by means of passive sampler in air, which involves the TD technique and the analysis by GC-MS; nevertheless, some results are presented with an FID detector, taking into account the similarities in terms of the results found in different studies.

FIGURE 6, in addition, allows us to observe the significant number of studies carried out by the carbon disulfide extraction method as a solvent, represented by the red triangles, and the implementation that has begun to be carried out in different parts of the world. The thermal desorption technique (TD) is represented in FIGURE 6 with yellow circles. It is noteworthy that although the technique of TD is not a new technique if has been optimized overtime and nowadays it has much better sensitivities than the solvent extraction technique.

3.3.3 Linearity

Linearity depends on the conditions of both the desorption process and the analysis process itself. The variables in the Thermal desorption system can cause the same regression process to have significant variations; TABLE 6 illustrates the variations in the linear regression for different studies in the BTEX analysis.

3.3.4 Working Range

The working range depends on the sensitivity of the analytical technique; so, for the preparation of the calibration curve, an analytical standard of 2000 $\mu g \cdot ml^{-1}$ is usually started. From this primary standard it is prepared a secondary standard (usually 100 $\mu g \cdot ml^{-1}$) and from this standard the liquid phase calibration curve is prepared. The usual working range for the analysis of BTEX by thermal desorption and GC-MS is from 0 to 350 $\mu g \cdot ml^{-1}$, as described in TABLE 7.

TABLE 6 – Variations in the linear regression for different research in the BTEX Analysis

Reference	Range	Benzene	Toluene	Ethylbenzene	m,pXylene	oXylene
Liaud et al. (2014)	R2	0.9890	0.9870	0.9900	0.9900	0.9840
Pandey and K.-H. Kim (2009a)	R2	0.9980	0.9990	0.9990	0.9990	0.9990
	R2	0.9960	0.9997	–	0.9999	–
Pilidis, Karakitsios and Kassomenos (2005)	R2	0.9983		–	0.9962	–
Cavalcante et al. (2010)	R2	0.9986	0.9987	0.9989	0.9990	0.9989
Du et al. (2013)	R2	0.9900	0.9900	–	0.9700	–
Pandey and K.-H. Kim (2009b)	20-80 R2	1.0000	0.9900	–	0.8600	
Y.-H. Kim and K.-H. Kim (2012)	R2	0.9999	0.9975	–	0.9921	–
–	No Report					

The values presented in the table were compiled from each of the indicated references

TABLE 7 – Variations in working range and Sensitibity for different research in the BTEX Analysis

Reference	Range	Benzene	Toluene	Ethylben.	m,p Xylene	o-Xylene
Liaud et al. (2014)	0-4 ng	360155x	411181x	46427x	785510x	407260x
	4-50 ng	404507x	456511x	547897x	894735x	457928x
Pandey and K.-H. Kim (2009a)	2-200 ng	95281.1x	10786x	–	10167x	–
Cavalcante et al. (2010)	7.50-3750 ng	0.039x –0.068	0.061x –0.127	0.061x –0.112	0.142x –0.211	0.054x –0.090
Du et al. (2013)	2-2400 ng	0.91x+1.42	0.96x+1.82	–	0.95x+1.42	–
Pandey and K.-H. Kim (2009b)	5-50 ng	20509x	20671x	–	22230x	–
Y.-H. Kim and K.-H. Kim (2012)	003-2.79 ng	2587x	21599x	–	3388x	–
–No Report						
The values presented in the table were compiled from each of the indicated references						
The values thus indicated were obtained as the product of the concentration of the standards injected in the calibration curve by the volume of injection						

3.3.5 Sensitivity

The constant ***m*** is called sensitivity and corresponds to the constant of proportionality between the signal and the concentration. This proportionality is useful over a restricted range of values. At very low concentration values, the signal is too small and is subject to great uncertainty. At very high values, the proportionality given in the linear regression equation obtained from the calibration curve may no longer be valid. Therefore, this model is used in very few cases.

TABLE 8 illustrates sensitivity values for BTEX found in different works around the world, using Thermodesorption (TD) as an extraction method and gas chromatography coupled to a mass detector (GC-MS) as identification and quantification method.

Sensitivity (slope of the linear regression) and the linear correlation coefficient (R^2) allows establishing the linearity of each of the calibration points.

TABLE 8 – Sensitivity for BTEX by TD and GC-MS

Reference	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Liaud et al. (2014) (a)	360155	411181	466427	785510	407260
Liaud et al. (2014) (b)	404507	456511	547897	894735	457928
Pandey and K.-H. Kim (2009a)	95281	10786	–	10167	–
Cavalcante et al. (2010)	0,039	0.061	0.061	0.142	0.054
Du et al. (2013)	0,91	0.96	–	0.95	–
Pandey and K.-H. Kim (2009b)	20509	20671	–	22230	–
Y.-H. Kim and K.-H. Kim (2012)	2587	21599	–	3388	–

– NO report.

a. For the mass range from 0 to 4 ng.
b. For the mass range from 0 to 50 ng.

The values presented in the table were compiled from each of the indicated references

3.3.6 Limit of Detection (LOD)

The values for the limit of detection (LOD) were calculated using the formula: LOD=[(3*s blank)/slope] of calibration graphs, where ***s*** Blank is the standard deviation of the ten blank values of the eight linear fits for the individual analyte of interest (see TABLE 9).

Alternatively, it was calculated as the product of the standard deviation of the number of replicates multiplied by the Student's t-value at the 99.9% confidence level (6 df, t = 3.14). 1 μL injection (mean of 35 pg·μL^{-1}) F-WS (the first calibration point).

3.3.7 Limit of quantification (LOQ)

The Limit of Detection (LOD) was evaluated as 3 times the signal to noise ratio ((S/N)·3) and Limit of Quantification (LOQ) as 10 times the signal to noise ratio ((S/N)·10). TABLE 10 summarizes the values reported for the limit of quantification (LOQ) in the determination of BTEX according to the references selected for the present investigation.

3.3.8 Accuracy

The accuracy was evaluated on 3 points; each one was injected 3 times. The method was considered accurate if the recalculated concentration was between 90% and 110% of the real concentration. Just accepted accuracy of 20% for the xylenes isomers quantified with GC-PID because they were not totally resolved.

TABLE 9 – Limit of detection (LOD) for method analytic TD and GC - MS

Reference	Benzene	Toluene	Ethylbenzene	m-Xylene	o-Xylene	specifications
Pandey and K.-H. Kim (2009a)	*4.41	*2.84	*2.01	*4.38	–	$\mu g \cdot m^{-3}$
	3.78	4.87	5.16	15	–	(nmol·mol^{-1})
Ezquerro et al. (2004)	0.54	0.87	0.36	1.11	0.80	$\mu g \cdot m^{-3}$ 24 hour
	0.13	0.15	0.21	0.36	0.14	$\mu g \cdot m^{-3}$ 4 weeks
Ras-Mallorquı, Marcé-Recasens and Borrull-Balların (2007)	1.4	0.66	0.11	1.1	0.08	$\mu g \cdot m^{-3}$
Cavalcante et al. (2010)	0.22	7.48	0.33	0.31	0.47	$\mu g \cdot m^{-3}$
Du et al. (2013)	8.4	6.1		7.4	11	$\mu g \cdot m^{-3}$
	36	48		18	12	ng
Strandberg et al. (2005)	0.018	–	–	–	–	$\mu g \cdot m^{-3}$ 24 hour
	0.002	–	–	–	–	$\mu g \cdot m^{-3}$ 7 days
Liaud et al. (2014)	*0.024	*0.009	*0.003	*0.007	*0.004	$\mu g \cdot m^{-3}$
	12,1	4.5	1.7	3.3	2.1	calculate pg
Mabilia et al. (2001)	0.1	–	–	–	–	$\mu g \cdot m^{-3}$
Pandey and K.-H. Kim (2009b)	*52.30	*48.56	–	*49.38	–	$\mu g \cdot m^{-3}$
	0.08	0.08	–	0.07	–	ng
	*0.28	*0.23	–	*0.19	–	$\mu g \cdot m^{-3}$
	0,04	0.05	–	0.06	–	ng
Y.-H. Kim and K.-H. Kim (2012)	*251	*167	*134	*127	*128	$\mu g \cdot m^{-3}$
	6.87	5.37	4.97	4.74	4.76	pg

– NO report.

The values presented in the table were compiled from each of the indicated references

* Values calculated at 25°C and 1 atm. Of pressure

TABLE 10 – Limit of Quantification (LOQ)

Reference	Benzene	Toluene	Ethylbenzene	m-Xylene	o-Xylene	specifications
Vichi et al. (2016)	0.4000	0.0900	–	0.1000	0.1400	($\mu g \cdot m^{-3}$)
Ras-Mallorquı, Marcé-Recasens and Borrull-Balların (2007)	1.6700	0.8300	0.1700	1.6700	0.1700	
C. Cocheo et al. (2009)	0.1800	0.1900	0.1900	0.2000	0.2100	

The values presented in the table were compiled from each of the indicated references

3.3.9 Precision

The ICH document in 2005 (GUIDELINE, 2005) establishes the guidelines for the validation process; according to this, the precision of an analytical procedure expresses the closeness of agreement (degree of scattering) between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions.

Precision may be considered at three levels: reproducibility, intermediate precision and repeatability.

Precision should be investigated using homogeneous, authentic samples. However, if it is not possible to obtain a homogeneous sample it may be investigated using artificially prepared samples or a sample solution.

The precision of an analytical procedure is usually expressed as the variance, standard deviation or coefficient of variation of a series of measurements.

3.3.9.1 Reproducibility

The objective of reproducibility is to verify that the method will provide the same results in different laboratories. The reproducibility of an analytical method is determined by analyzing aliquots from homogeneous lots in different laboratories with different analysts. In addition, typical variations of operational and environmental conditions that may differ from, but are still within, the specified parameters of the method are used.

An essential criterion in the quality control (QA) is the reproducibility of all calibration techniques, which were evaluated in terms of Relative Standard Deviation (RSD) values. The results shown in TABLE 11 allow illustrating the range of variability of the Precision for the method of passive sampling, extraction by thermal desorption and analysis by GC-MS.

TABLE 11 – Precision for passive sampling, thermal desorption and analysis GC-MS

Reference	Benzene	Toluene	Ethylbenzene	m,p-Xylene	O-xylene	Specificat.
Ezquerro et al. (2004)	6.60	8.10	10.30	9.60	12.80	–
	15.20	15.00	11.40	11.10	12.80	–
Strandberg et al. (2005)	1.00	–	–	–	–	Radiello Ca24
	6.00	–	–	–	–	Radiello Ca7D
	9.10	–	–	–	–	Radiello C524
	8.00	–	–	–	–	Radiello C57D
Liaud et al. (2014)	1.50	1.90	1.60	1.30	1.20	CV 5 ppb DI
	6.30	5.00	4.70	4.30	4.80	CV 5 ppb Spik
Pandey and K.-H. Kim (2009b)	3.80	2.60		14.00	–	–
Y.-H. Kim and K.-H. Kim (2012)	1.66	2.51	1.77	1.71	1.02	TIC Base
	1.92	1.61	1.40	1.14	0.46	EIC base

The values presented in the table were compiled from each of the indicated references

3.3.9.2 Repeatability

Repeatability applied in the same operational conditions during a short time interval was expressed as the relative standard deviation (RSD). It is important to assess the repeatability of at least two parameters in the gas chromatographic method: the retention time (confirming the identity of the analyte of interest) and the peak area or height (quantifying the analyte of interest). The repeatability of the method ranged from 5.62 to 9.63% of the peak area (quantitative analysis) and from 0.02 to 0.19% of the retention time (qualitative analysis), showing satisfactory precision (TABLE 12). Intra-day repeatability, expressed as RSD, was also evaluated during two consecutive weeks and no significant alteration was observed.

TABLE 12 – Repeatability for passive sampling, thermal desorption and analysis GC-MS

Reference	Benzene	Toluene	Ethylbenzene	mpXylene	Oxylene	Specifications
Ras-Mallorqui, Marcé-Recasens and Borrull-Ballarin (2007)	1.4	0.1	0.4	0.2	0.4	100 ng (n=3)
	15.2	15	11.4	11.1	12.8	
Cavalcante et al. (2010)	7.93	5.62	8.15	8.19	7.95	
Du et al. (2013)	7.3	8.5		7.4	4.9	
Liaud et al. (2014)	1.5	1.9	1.6	1.3	1.2	CV 5 ppb DI
	6.3	5	4.7	4.3	4.8	CV 5 ppb spik
Pandey and K.-H. Kim (2009b)	3.8	2.6		14		
Y.-H. Kim and K.-H. Kim (2012)	1.66	2.51	1.77	1.71	1.02	TIC Base
	1.92	1.61	1.4	1.14	0.46	EIC base
C. Cocheo et al. (2009)	6.7	8.6	8.8	8.9	9.1	Radiello 7 day

The values presented in the table were compiled from each of the indicated references

3.3.10 Uncertainties of measurement

According to Du et al. (2013) the biases of these method are below 5% for all the compounds while the ranges of the repeatability of Tsinghua Passive Diffusive Sampler (THPDS) samplers are 7.9–12.5% with an average of 10.5% for Benzene, 6.7–15.2% with an average of 10.5% for Toluene, and 3.6–11.7% with an average of 7.4% for Xylenes. Consequently, the overall expanded uncertainties (%) of THPDS samplers under field test at 95% confidence level are 21.5%, 23.3% and 16.9% for Benzene, Toluene and Xylenes, respectively, meeting the requirement of NOISH protocol. This is mainly from the variation of sampling rates due to the effect of environmental factors and the random error of determination of the adsorbed masses by ATD-GC/MS.

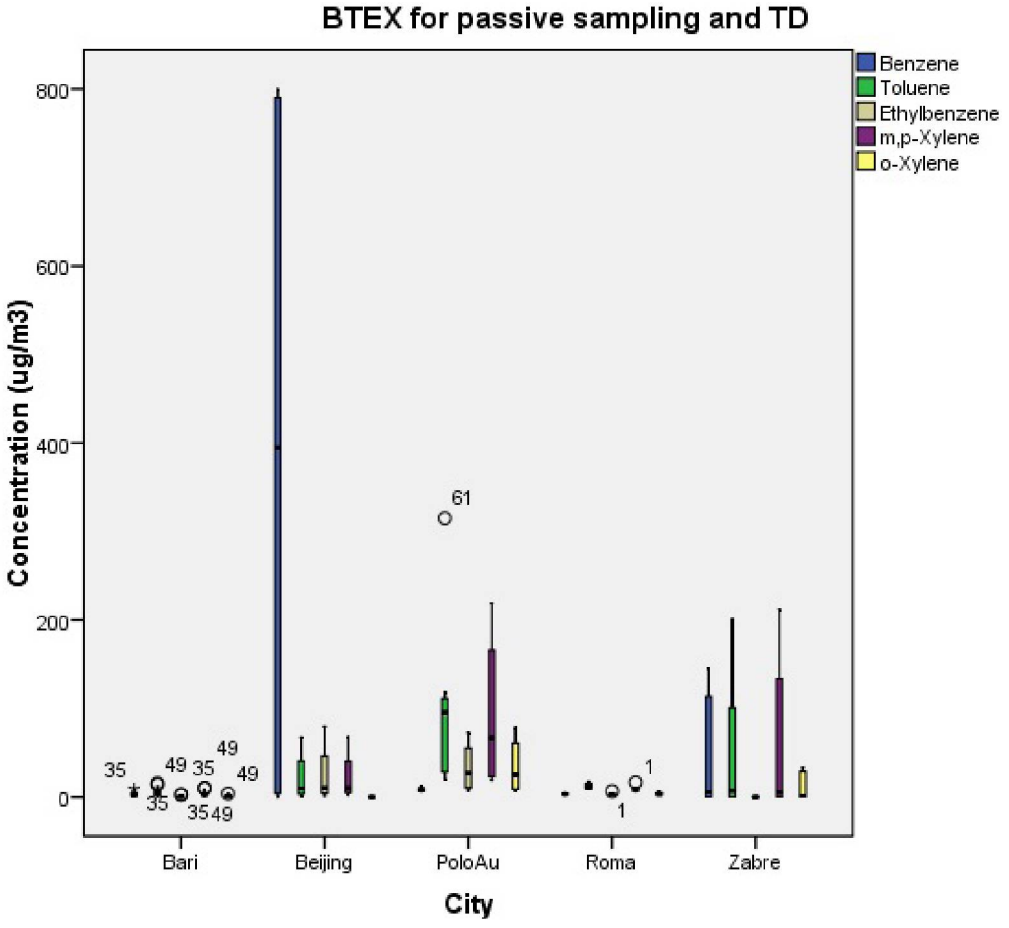
TABLE 13 – Estimation of measurement uncertainties of the thermally desorbable Radiello using the active (pumped) method as reference (ISO 13752)

Compound	Model parameters	Concentration $\mu g \cdot m^{-3}$	U(p=0.95) $\mu g \cdot m^{-3}$	U(p=0.95) (%)
Benzene	b0± sb0=0,298±0,233	2.4	0.44	18.2
	b1±sb1=0,991±0,059	14.3	2.60	18.2
Toluene	b0± sb0=2,788±0,881	9.1	3.64	40.0
	b1±sb1=0,851±0,447	48.1	9.14	19.0
Ethylbenzene	b0± sb0=0,031±0,322	1.9	0.78	41.0
	b1±sb1=0,992±0,087	9.1	1.70	18.7
m,p-xylene	b0± sb0=0,0219±0,823	6.9	1.92	27.8
	b1±sb1=0,980±0,062	32.9	4.19	12.7
o-Xylene	b0± sb0=1,214±1,141	2.0	1.57	78.4
	b1±sb1=0,943±0,063	12.1	2.57	21.2

C. Cocheo et al. (2009) in 2001 conducted an investigation with the objective of field evaluation of thermal and chemical desorption BTEX radial diffusive sampler

Radiello (TABLE 13). In this investigation expanded uncertainty of BTEX determination under field conditions was determined. The ISO 13752 standard has been used to evaluate the uncertainty of the Radiello BTEX measurements under field conditions using the active (pumped) sampling method as reference. In this standard the values of the reference method (x-method) are assumed to be 'true values' while the method (Radiello) whose uncertainty is under investigation (y-method) is assumed to be the 'test method'. All differences between the measurements carried out with test and reference methods are attributed to measurement deviation of the test method. As the uncertainty of the reference method is not taken into account by the statistical procedures described in the standard, this approach could lead to an overestimation of the uncertainty of the test method. Thus, all the uncertainties that will be attributed to the test method can be assumed as an overestimation of the true ones. The table illustrates the uncertainties found for one of the BTEX's constituent compounds.

FIGURE 7 – Cities that present BTEX sampling with the technique of passive sampling and thermal desorption of the analytes



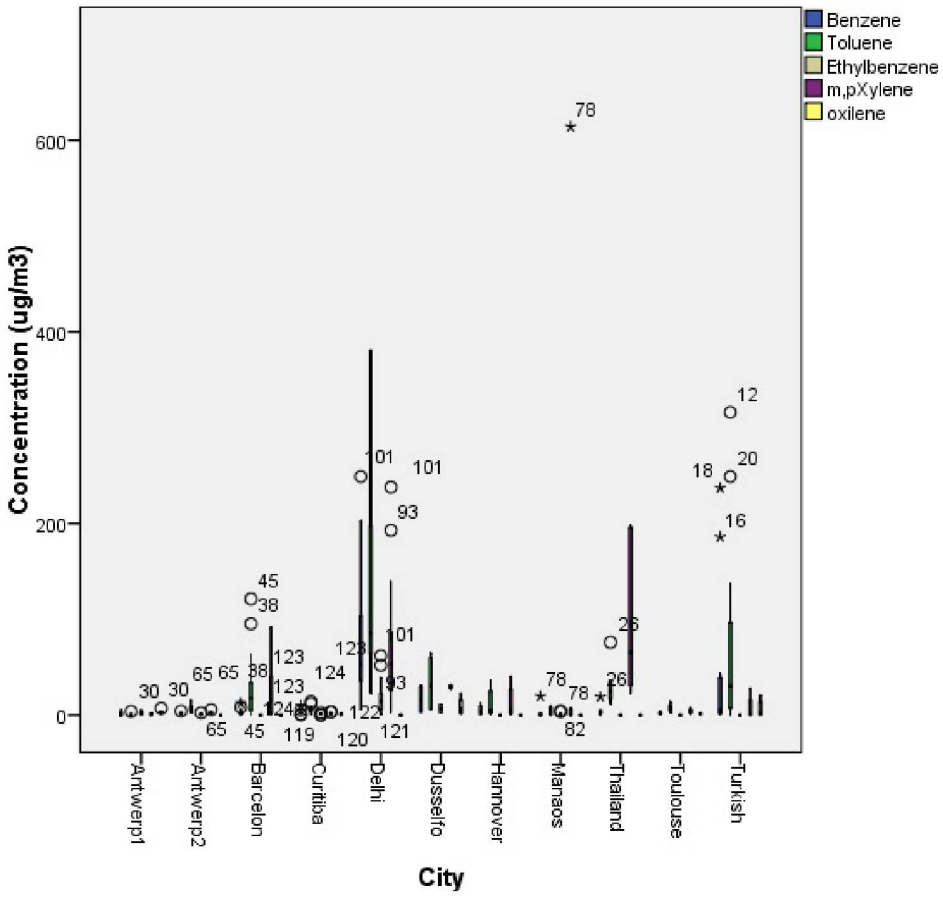
SOURCE: Mabilia et al. (2001),Pyta (2006),Brodzik et al. (2014)Caselli et al. (2010),Jiang et al. (2013)

3.3.11 Reported data of BTEX using passive diffusive sampler, thermal desorption and chromatographic analysis.

The following are the studies (see FIGURE 7) found for the analytes of interest based on the literature review. Studies carried out in the cities of Rome Italy (MABILIA et al., 2001), Zabrze Poland (PYTA, 2006), Bari Italy (CASELLI et al., 2010) and Beijing China (JIANG et al., 2013) are examples of the application of BTE sampling in air, using the diffusive passive sampling system coupled to the thermal desorption of the sample and analysis by gas chromatography with mass detector.

The results illustrated in FIGURE 7 are concordant with the population and the number of sourcing in each of the cities under study. The highest average concentrations were recorded in Beijing, which has a growing population of around 21.71 million inhabitants, while the lowest concentrations of BTE were registered in Bari with a constant growth rate.

FIGURE 8 – Cities that present BTEX sampling with the technique of passive sampling and solvent desorption (CS_2) of the analytes



SOURCE: (MABILIA et al., 2001),(PYTA, 2006),(CASELLI et al., 2010),(JIANG et al., 2013)

As part of the literature review, a summary of the results obtained by the

technique of liquid extraction with carbon disulfide and analysis by chromatography with both (FID) and (MS) detector are presented in the FIGURE 8.

According to Harper (2000) Carbon disulfide is a good solvent for non-polar compounds. It elutes rapidly at the front of the analysis on most common GC columns, and has a very low response on a flame ionization detector. This combination of qualities has made carbon disulfide the most popular solvent for this kind of analysis. However, it can react with certain compounds (e.g., amines), and can interfere with the analysis of certain volatile chlorinated hydrocarbons. Carbon disulfide is not suitable for electron-capture detectors. It is highly toxic and has an objectionable odor.

The desorption efficiency of analytes from charcoal using carbon disulfide depends on the type and quantity of analyte, the types and quantities of other collected chemicals, especially water vapor, the amount of sorbent, and the amount of solvent.

According to Harper (2000) Thermal desorption (TD) has an advantage over solvent desorption in the lesser quantities of solvents used, with consequent implications for laboratory safety and waste disposal. However, the main advantage of TD, as previously mentioned, is the enhanced sensitivity that can be achieved. In many situations, this factor alone compensates for the higher cost of the analysis. Two examples of the difference in sensitivity between thermal and solvent desorption are illustrated in FIGURE 9.

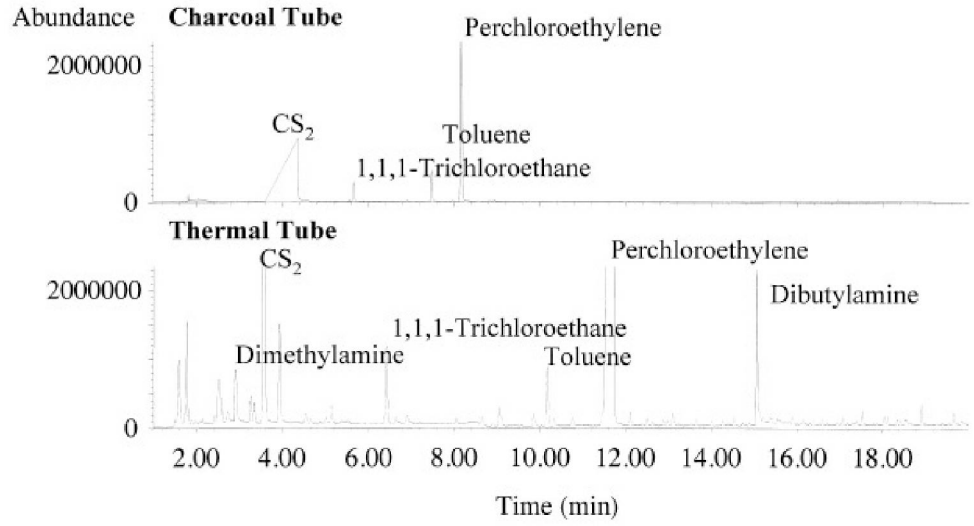
3.4 METHODS FOR BTEX ANALYSIS

The BTEX analysis comprises two types of methods: automated and manual. These two types of methods have two different principles that can be applied to air quality monitoring. The automated method allows online measurements, which can be made along an optical path. The manual measurements involve the collection of samples in the field and a subsequent analysis in the laboratory. Skov, Lindskog, et al. (2001) establish that the most widely used online method is the Differential Optical Absorption Spectroscopy (DOAS), which is an open-path optical measurement technique based on the differential absorption of ultraviolet or visible light, however, they claim that currently, the DOAS method is not completely validated, and the limit of detection is relatively high (1 $\mu g{\cdot}m^3$).

Manual measurements with sample collection in the BTEX field are based on the absorption of air samples in cartridges of different absorbents or in their capture and storage in canister. Once the samples are taken to the laboratory they require a desorption procedure, in the case of the cartridges, or their analysis by direct injection in the case of canister.

The air samples are collected at the site and then analyzed, either directly in an

FIGURE 9 – Difference in sensitivity between solvent and thermal desorption



SOURCE: (HARPER, 2000)

NOTE: Samples taken from a factory producing rubber moldings. Solvent desorption samples were collected on 100 mg front-section charcoal tubes (note amines not detected by this procedure). Thermaldesorption samples were collected on Carbotrap C–Carbotrap B–Carboxen 569 multi-bed tubes. Analysis on 30 m 30.25 mm I.D. DB-1 column (1 mm film thickness) in a Hewlett-Packard 5890 GC system with HP 5970 mass-selective detector

automated GC in the field, or offline in a central laboratory. The two principles represent different practical operating conditions where, for example, different calibration systems and quality control strategies must be applied.

In general, the analysis of the samples is carried out both for samples desorbed and for those injected directly by Gas Chromatography (GC) with different detectors, for example, Flame Ionization Detector (FID), Photoionization Detector (PID) or Mass Spectrometer detector (MS).

3.5 BTEX SAMPLING METHODS

3.5.1 Automated GCs

Skov, Lindskog, et al. (2001) states that BTEX in ambient air are often measured by BTEX monitors, which are automatic GCs specially designed to measure only these compounds in situ. However, the principle is the same for laboratory GCs as for BTEX monitors. The advantage of BTEX monitors is that the time series can be obtained with a high time resolution, usually 15 to 30 minutes, and therefore the data can be compared and interpreted. Taking into account that BTEX monitors work automatically it is possible to establish online data transmission, as well as verify the status of the

instrument through a modem.

According to Skov, Lindskog, et al. (2001) the main disadvantages are that a constant working temperature is required, for example a cabin controlled by thermostat, which generates high costs to establish a monitoring network with BTEX monitors even though the operational cost is relatively low.

3.5.2 Manual methods

Different manual sampling techniques are used to sample hydrocarbons from the atmosphere. The techniques are described below. Common to all of them is that samples are taken in the field and then they are transported to a central laboratory for analyzing. In this way, one GC can be used to analyze samples from an entire monitoring network, thus reducing the effective cost compared to a system with BTEX monitors. However, the running price of the network is much higher as these methods are more labor-demanding (except for diffusive samplers). Skov, Hansen, et al. (2001) mentions the following sampling methods:

3.5.2.1 Canister

Canisters details that Canister sampling is performed in two ways: either as in bags of Tedlar type sampling or as pumped sampling. After sampling, the canisters are brought to the laboratory, where they are evacuated through a cold trap or cryo-trap. The preconcentrated sample is finally introduced into a GC for analysis by ballistic heating of the trap in a flow of carrier gas. Canisters are widely used for hydrocarbon measurements in ambient air. This technique of sampling is especially useful for the most volatile non-reactive species, such as propane, butane, etc (SKOV; HANSEN, et al., 2001).

3.5.2.2 Pumped tube sampling

Pumped tube sampling: The principle for manual pumped sampling is the same as for automated GCs. Air samples are sucked through an adsorbing cartridge. The sampling pump must be calibrated and applied following the European Standard, EN 1232 (1993). Many different adsorbing materials are used with various sampling efficiencies towards hydrocarbons and with multiple efficiencies of thermal desorption (WOOLFENDEN, 1997; HARPER, 2000). The most reliable adsorbing material is activated charcoal, in which case solvent extraction usually must be applied, using, for example carbon disulfide (COURSIMAULT; DONATI; VIELLARD, 1995; W. HEINRICH, 1997). The resulting extract is analyzed by a standard GC.

3.5.2.3 Diffusive sampling

Diffusive sampling: The principle of diffusive sampling is the uptake of compounds on a cartridge described by Fick's 1st law (F= -DdC/dx), where F is the flux, D is the diffusion coefficient, C is the concentration and x is the diffusion path length). As for pumped tube sampling, solvent extraction is needed when activated charcoal is used as the adsorbent (C. COCHEO et al., 2009; W. HEINRICH, 1997). When thermal desorption is used a weaker adsorbent must be applied (BROWN; PURNELL, 1979).

Within the diffusive samplers, commercially available, it stands out Perkin-Elmer tubes adsorb hydrocarbons by axial diffusion, and the uptake rate is around 1 ml·min^{-1} (BROWN; CHARLTON; SAUNDERS, 1981; BROWN; WRIGHT; PLANT, 1999). Alternatively, radial diffusion is used, e.g., in the Radiello tubes, which have an uptake rate of about 80 ml·min^{-1} using activated carbon as adsorben (C. COCHEO et al., 2009). Even though there is much more significant uptake rate for the Radiello tubes, the possible time resolution is almost the same as for the Perkin-Elmer tubes, as a lot of sensitivity is lost in the solvent extraction step. However, Radiello tubes with other adsorbents suitable for thermal desorption have recently become available. Also, Uchiyama and Hasegawa (2000) have presented a new radial diffusive sampler, where the sample can be analyzed by thermal desorption-GC.

3.6 BTEX EXTRACTION METHODS

3.6.1 Solvent extraction method

Point measurements of BTEX are performed in most case, a solvent extraction method followed by chromatographic analysis. Solvent extraction method shows an excellent efficiency, repeatability, and compatibility with most of the adsorbents, especially with activated charcoal, which is widely used in the occupational health field because of its low cost and broad compatibility with organics. Harper (2000) concludes that these methods require analytical preparation steps, which imply delays, costs (price of solvents and standards, analyst work time) and possible manipulation mistakes (broken samples, cross-contamination, etc.). Moreover, the toxicity of the commonly used solvents (dichloromethane, carbon disulfide, etc.) represents an obvious safety and sanitary health risk which implies important precautions for the operators, and an environmental problem requiring constraining and expensive recycling processes.

3.6.2 Thermal desorption extraction method - TD

Candelier et al. (2011) says that the analytical technique of thermal desorption or thermodesorption, coupled to different detectors, allows the analysis of volatile and semi-volatile organic compounds directly from small sample sizes without the need for

extraction with toxic solvents or other steps of sample preparation, which reduces the risks of product loss, environmental emissions and the occupational risk of analysts.

The thermodesorption phase is divided into two steps: a first step with respect to the thermal treatment in an inert atmosphere, during which volatile and semi-volatile products are formed and trapped resulting from the extraction of the compounds of interest from the sample analyzed in a specific adsorbent, known as trap. The recovery of adsorbed compounds is based on the different shape of adsorption isotherms at different temperatures.

A second step during which the sample concentrated in the trap is desorbed at high heating rates and keeping the trap at high temperatures, thus transferring all the compounds of interest to the column for normal chromatographic analysis. The use of thermal desorption requires, therefore, an accurate preliminary investigation of the adsorbed compound - adsorbing medium pair. Stronger adsorbents are suitable for very volatile compounds but will yield only partial desorption of heavier compounds.

Diffusive samplers require a relatively long sampling time, which makes them less suitable for process studies. On the other hand, diffusive samplers do not need electrical power, and therefore, they are well fitted to measurements of geographical distributions, human exposure (V. COCHEO; SACCO, et al., 2000; SKOV; HANSEN, et al., 2001) and they are very cost efficient for analyses of long-time trends (SVANBERG; GRENNFELT; LINDSKOG, 1998).

3.7 CRITICAL ANALYSIS

During the development of this chapter, the different air pollutants have been presented, and the great importance that VOCs in general and specific components of VOCs, such as BTEX in particular, have in relation to their health impacts on the exposed population.

The proven carcinogenic effects of BTEX and its fundamental contribution to the formation of other types of pollutants justify its research, especially because through this chapter the innumerable sources that originate this class of compounds were presented.

Once the need for the sampling of these compounds is justified, the different methodologies used in the sampling are presented, and a special reference is made to the passive sampling methods because of their importance for the reduction of costs in the same sample, and for the relevance that this type of samplers has in the evaluation of the exposure of the human population.

Once again special emphasis is placed on the thermal desorption technique, and again for its significant advantages in terms of technical costs, the elimination of toxic solvent uses and the possibility of reuse of passive samplers, using thermal

desorption, which again makes one of the most cost efficient techniques currently available.

Finally, because the analytical technique was used for the first time in the air quality laboratory of the Federal University (UFPR), it is necessary to validate the analytical technique following the recommendations of Inmetro in the Guidance document for orientation on validation of analytical methods DOQ-CGCRE-0008 in its revision of August 5, 2016 and the standards incorporated in ABNT NBR ISO / IEC 17025. So the following is the development of the validation of the analytical technique for BTEX determination in samples of ambient air, by passive sampler, following the EPA Method TO-15, and using the thermal desorption (TD) technique and GC analysis with mass detector (MS).

4 THE NEW METHODOLOGY APPROACH USING THERMAL DESORPTION

Instrument qualification means that the specifications are defined, tested and confirmed so that the instrument is suitable for the methods to be validated. The analytical methods are then validated on qualified instruments to prove that the method works as intended. A specific instrument is then combined with a specific method to run system-suitability tests. System suitability parameters should be selected during method validation. Successful system suitability test runs to ensure that the complete system meets the analyst's expectations under the specific conditions of the tests. The highest level of testing is the analysis of quality control of the samples. Standards or samples with known amounts are analyzed and the results compared with the known amounts.

Method validation occurs between analytical instrument qualification and system suitability testing and is linked to all other quality elements. Methods should be validated using qualified instruments. During method validation, parameters and acceptance criteria for system suitability checks and quality control checks should be defined.

Analytical method validation is essential for Good Laboratory Practice (GLP) regulations (ABNT NBR ISO/IEC 17025:2005). The DOQ-CGCRE-008 cGMPs spell out the requirements for validation in section 8: “The accuracy, sensitivity, specificity, and reproducibility of test methods employed by the firm shall be established and documented".

Such validation and documentation may be accomplished by DOQ-CGCRE-008: Laboratory records should include a statement of each method used in the testing of the sample. The statement shall indicate the location of data that establish that the methods used in the testing of the sample meet proper standards of accuracy and reliability as applied to the product tested. The suitability of all testing methods used shall be verified under actual conditions of use.

DOQ-CGCRE-008 section 8: Complete records shall be maintained of any modification of an established method employed in testing. Such records shall include the reason for the modification and data to verify that the modification produced results that are at least as accurate and reliable for the material being tested as the established method.

According to ISO 17025, analytical methods should be validated through laboratory tests: “Validation of an analytical procedure is the process by which it is established, by laboratory studies, that the performance characteristics of the procedure meet the requirements for the intended analytical applications”. In an attempt to standardize,

representatives from the industry and regulatory agencies from the United States, Europe, and Japan defined parameters, requirements, and methodology for analytical methods validation through The International Conference for Harmonization (ICH). The parameters, as defined by the ICH and other organizations and authors, are summarized TABLE 14 and are described in the following paragraphs.

TABLE 14 – Parameters for method validation with reference to ICH, USP and ISO 17025 - (GUIDELINE, 2005)

Parameter	**Comment**
Specificity	USP, ICH
Selectivity	ISO 17025
Precision	USP, ICH
Repeatability	ICH, ISO 17025
Intermediate precision	ICH
Reproducibility	ICH, defined as ruggedness in USP, ISO 17025
Accuracy	USP, ICH, ISO 17025
Linearity	USP, ICH, ISO 17025
Range	USP, ICH
Limit of detection	USP, ICH, ISO 17025
Limit of quantitation	USP, ICH, ISO 17025
Robustness	USP, Included in ICH as method development activity, ISSO
Ruggedness	USP, defined as reproducibility in ICH
Source: ICH Q2A, Validation of Analytical Procedures: Definitions and Terminology, Geneva, 1995, in 2005 incorporated in Q2(R1)	

This research reviews the performance in validating quantitative analytical method, in special of the measurement of BTEX in the air, for which the proposed methodology is the METHOD EPA TO-15 Determination of Volatile Organic Compounds (VOCs) in Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS).

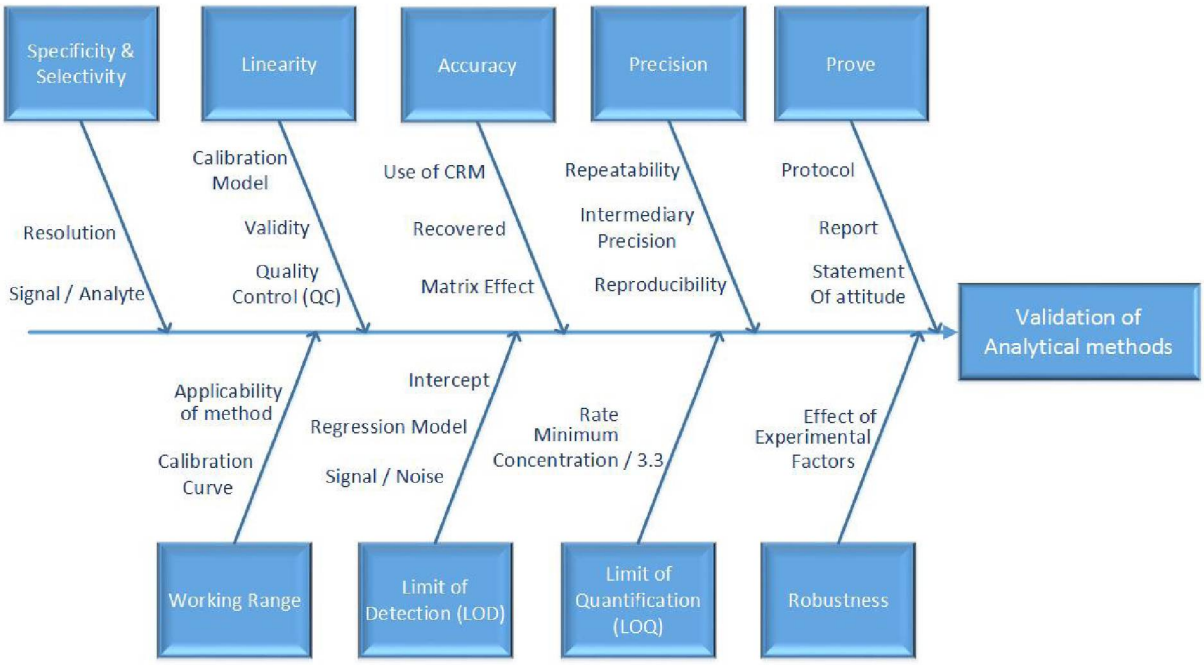
After introducing the scope of this quantitative method, their main characteristics will be discussed: the institutions, programs, and documents dealing with the validation of quantitative methods, and the performance parameters were presented - Specificity/Selectivity, Precision, Accuracy and Recovery, Linearity and Calibration Curve, Range, Limit of Detection, Limit of Quantitation, Ruggedness, Robustness. The various strategies used to validate this quantitative analytical method were also be briefly described — Contingency Tables, Bayes' Theorem, Statistical Hypothesis Tests and Performance Characteristic Curves. In addition, in the following chapters, the conditions

for each of the items related in TABLE 14 are specified, FIGURE 10 summarizes the general stages of the validation process.

4.1 VALIDATION OF THE BTEX ANALYTICAL TECHNIQUE

The diagram FIGURE 10 summarizes the validation process of an analytical technique. The validity of a specific method should be demonstrated in laboratory experiments using samples or standards that are similar to unknown samples analyzed routinely (see FIGURE 10). The preparation and execution should follow a validation protocol, preferably written in a step-by-step instruction format. This chapter describes the approach and steps to validate standard analytical procedures and methods (METHOD EPA TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Cartridge and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS).

FIGURE 10 – validation process of an analytical technique



SOURCE: (DELGADO, 2009)

The analytical methods hereafter described will be set up with the Perkin-Elmer Turbomatrix thermal desorber and gas chromatograph (ATD-TD/GC) (Perkin Elmer Clarus 680) coupled to a mass spectrometer (Perkin Elmer Clarus SQ 8 T Perkin Elmer - Waltham, USA), the equipment belonging to the "Laboratory of Analysis and Quality of Air" - LAB AIR of the program of Environmental Engineering of the Federal University of Paraná. In the following, we will propose the method for BTEX analysis. This method is suited to outdoor sampling in urban monitoring, where the investigation is usually focused on Benzene, Toluene, Ethylbenzene and Xylene isomers. The methods

developed for the determination of VOCs present similar characteristics to those of BTEX. The two methods differ by a few details, such as the higher desorption temperature for VOCs and the higher cryofocusing temperature for BTEX (see FIGURE 10). The latter caution is introduced to avoid freezing of excess humidity gathered during the sampling in the cryofocusing trap. The conditions under which the samples are run in the gas chromatograph are as follows:

TABLE 15 – Optimization System Thermo desorption - Perkin Elmer ATD Turbomatrix 300

Temperatures (℃)		**Timing (min)**		**Pneumatics (PNU)**	
Transfer	230	Purgue	1,0	Column Press	14.8 psi
Valve	220	Desorb	12.0	Outlet Split	20 ml·min^{-1}
Tube	320	Trap Time	16.5	Inlet Split	20 ml·min^{-1}
Rate low	10	Total Time	30.0	Desorption	100 ml·min^{-1}
Rate High	325			Trap Press	8.0 psi
Trap	100℃·s^{-1}				

Column: Rxi 624 Sil MS - Restek: 95% dimethylpolysiloxane, length 30 m, i.d. 0.32 mm, film thickness 1.8 μm; the column is directly fitted to the six-port valve of Turbomatrix apparatus. Temperatures GC oven: 50℃ for 1 minute, 16℃·min^{-1} up to 90℃, maintain for 1 minute, 2.5℃·min^{-1} up to 100℃, maintain for 1 minute, 30℃·min^{-1} up to 250℃ final isotherm 4.5 minutes. GC-MS interface: 270℃, Flows Carrier gas: Helium, 1.2 ml·min^{-1}

4.1.1 Specificity and Selectivity

A sample, in general, consists of the analytes to be measured, the matrix, and other components that may have some effect on the measurement, but can not be quantified. Specificity and selectivity are related to the detection event, and the method that produces a response to only one analyte is called specific. A method that provides answers to various analytes, and at same time can distinguish the response of one analyte from another one, is called selective. For the purposes of the present study and taking into account that the analysis was done by gas chromatography, and considering that gas chromatography allows distinguishing the response of each the BTEX and differentiating them from each other, for which reason the present method as selective.

The Radiello diffusive sampler (F.S. Maugeri, Padova, Italy) has been developed recently (V. COCHEO; BOARETTO; SACCO, 1996). It consists of a coaxial cylindrical cartridge filled with an adsorbent housed in a porous polyethylene diffusive body. The large diffusive surface area allows a high sampling rate, making the sampler suitable

for both short (24 h) and longer periods (one week) of air sampling (V. COCHEO; BOARETTO; SACCO, 1996; BOMBOI et al., 2002; ANGIULI et al., 2003). Radiello samplers have been used for stationary monitoring as well as personal sampling at varying concentrations of VOCs (CREBELLI et al., 2001; SKOV; HANSEN, et al., 2001). The new badge-type sampler SKC-Ultra (SKC Inc.) is compatible with thermal desorption, thus improving the sensitivity. Moreover, its size and shape make it appropriate for personal sampling.

Strandberg et al. (2005) found that Comparison of adsorbents and samplers uptake rates were approximately 26 times higher (for both compounds) using the SKC-Ultra with CaX, and about 50 and 40 times higher for benzene and 1,3-butadiene, respectively, using the Radiello with CaX, than published rates obtained using a traditional approach with PE tubes and CaX adsorbent (MARTIN; MARLOW, et al., 2003; MARTIN; DUCKWORTH, et al., 2003). For the SKC-Ultra sampler, no uptake rates have yet been published. Uptake rates (over 24 h) of 80 mL·min^{-1} for Benzene have been reported for the Radiello sampler containing activated charcoal (V. COCHEO; BOARETTO; SACCO, 1996) and confirmed in field studies, in which the results were compared to data obtained with a pumped system (ANGIULI et al., 2003). The Radiello data, obtained using graphitized carbon black adsorbents, were between a half and a third of the cited rates, but were nonetheless much higher than those obtained using the tube-type PE sampler, for which, in the present investigation, the adsorption systems will be used, through passive sampling, of greater selectivity and sensitivity known in the market.

4.1.2 Linearity

Linearity is the ability of an analytical method to produce results that are directly proportional to the analyte (see Equation 4.1) concentration in samples in a given concentration range. Quantification requires that the dependence between the measured response and the analyte concentration be known. Linearity is obtained by internal or external standardization and is formulated as a mathematical expression used to calculate the analyte concentration to be determined in the actual sample. The equation of the line that relates the two variables is:

$$y = mx + b \tag{4.1}$$

Where: y = measured response (height or peak area); x = concentration; m = inclination of the calibration curve = sensitivity; b = intersection with the y-axis, when x = 0.

The linearity of a method can be observed by the graph of the test results as a function of the analyte concentration or else calculated from the linear regression

equation determined by the least squares method.

Calibration curves are obtained, for the present investigation, by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece (10 cm) of wide-bore (0.53 i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16"- 1/4"). The 1/4" Swagelock is equipped with a PTFE ferrule instead of the original steel one; A after that, a blank cartridge was introduced in a Turbomatrix tube and fit the tube to the Swagelock nut. The injector was maintained at 200℃ but the GC oven was not heated. 1 μl of each calibration solution was inject slowly under nitrogen flow (50 ml·min^{-1}) and the system was let to purge for 2 minutes. Next, the cartridge was analyzed in the same manner as the samples. The following step was preparing a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 8, 4, 2, 1, 0.04, 0.02 and 0.01 μg·$\mu.l^{-1}$ of each compound, analyzing each in quintuplicate.

The linear correlation coefficient (***R***) is often used to indicate how straight a line can be considered as a mathematical model. It is advisable to evaluate homoscedasticity (homogeneity of variables)

As linearity deviations are often difficult to detect visually, their adequacy can be verified by calculating the residuals between the measured values and the values calculated from the equation regression analysis. The value of ***t*** is calculated by:

$$t_{calculated} = \frac{residual}{S_r\sqrt{n}} \tag{4.2}$$

Where:

- Residual: $X_{average}$ - $X_{calculated}$
- S_r: standard deviation of the residues
- n = number of points

If the value of ***t*** calculated for a doubtful point on a calibration curve is less than or equal to the unilateral ***t*** value, for the desired confidence and (n-1) degrees of freedom, the point is considered to belong to the curve and range up to it is linear.

Most of the existing detection equipment establishes its linear dynamic range. It is necessary, however, to verify to what extent the concentration range of the analyte coincides with the linear dynamic range and to ensure that no other phenomenon has an undesirable impact on the response.

Some analytical procedures do not demonstrate linearity even after any transformation. In these cases, the analytical response can be described by a suitable function of the analyte concentration in the sample.

4.1.3 Working range and linear working range

For any quantitative method, there is a range of analyte concentrations or property values at which the method can be applied.

At the lower limit of the concentration range, the limiting factors are the limits of detection and quantification. At the upper limit, the limiting factors depend on the response system of the measuring equipment. Within the working range there may be a linear response range and within this, the signal response will have a linear relationship with the analyte or property value. The extent of this range can be established during the evaluation of the working range.

The linear working range of a test method is the interval between the lower and upper levels of analyte concentration where it has been demonstrated that determination with the required accuracy, precision and linearity is possible under the conditions specified for the test. The linear range is defined as the range of concentrations at which the sensitivity can be considered constant and is normally expressed in the same units of the result obtained by the analytical method.

For the purposes of the present investigation, the range of work will be established based on the recommendations of the supplier of the sampling cartridges-Radiello who recommends concentrations in the range of 0.01 to 8 μg·μl, within this range determine the linear range of work from the linear regression analysis.

4.1.4 Sensitivity

The sample array may contain components that interfere with the performance of the measurement by the selected detector, without causing a visible signal in the specificity test. Interferences may increase or decrease the signal, and the magnitude of the effect may also depend on concentration.

Various tests and their corresponding statistics can be used for the study of selectivity depending on the availability of the analyte, the matrix without the analyte and reference samples at the concentrations of interest. If the matrix of the sample without analyte or a satisfactory group of reference samples is available, it will be applied for the BTX analysis, the F (Snedecor) tests of homogeneity of variances and the test t (Student) of comparison of averages, or else performed the analysis of the deviations from the reference values. It is hypothesized that the matrix does not affect the analyte signal at high or above range levels. Two groups of samples will be prepared, one with

the matrix and the other without, both groups with the concentration of the analyte identical at each concentration level of interest. The number of parallel samples at each concentration level will be 10 (ten) to allow proper use of the statistical models and provide a valid comparison. First the F test will be performed to verify if the variances of the samples can be considered equal, calculating:

$$F_{calculated} = \frac{S_1^2}{S_2^2} \tag{4.3}$$

Where S_1^2 and S_2^2 are the variances of each sample, with the most significant variation in the numerator. At the same time, the value of ***F*** tabulate is obtained, with (n_1-1) degrees of freedom in the numerator and (n_2-1) degrees of freedom in the denominator; usually, a 95% confidence level is adopted. There are two cases:

1. if ***F*** calculated is less than the tabulated ***F***, the variances can be considered equal, that is, the matrix does not have a significant effect on the accuracy of the method in the concentration range under study. In this case, the standard deviations of the test groups can be grouped and the equality of the means of the two sets of samples can be tested with the Student t distribution

2. If calculated ***F*** is higher than the tabulated ***F***, the variances cannot be considered equal, that is, the matrix has a significant effect on the precision of the method in the concentration range under study, and the calculated value is:

$$t_{calculated} = \frac{\left|\overline{X_1} - \overline{X_2}\right|}{\sqrt{\frac{S_1^2}{n_1} - \frac{S_2^2}{n_2}}} \tag{4.4}$$

In this case, to obtain the tabulated ***t***, the number of degrees of freedom (ϑ) is equal to:

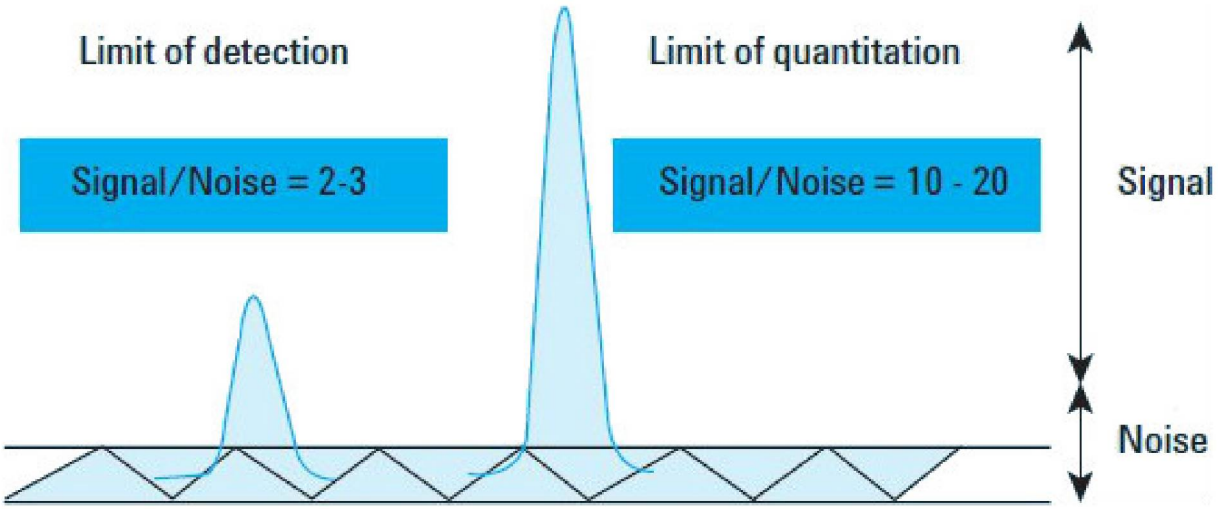
$$\vartheta = \frac{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}\right)}{\frac{\left(S_1^2\right)^2}{n_1+1} + \frac{\left(S_2^2\right)^2}{n_2+1}} \tag{4.5}$$

4.1.5 Limit of Detection (LOD)

International Conference for Harmonization (ICH) defines the detection limit of an individual analytical procedure as the lowest amount of analyte in a sample, which can be detected but not necessarily quantified as an exact value. The limit of detection (LOD) is the point at which a measured value is larger than the uncertainty associated with it. It is the lowest concentration of an analyte in a sample that can be detected

but not necessarily quantified. The limit of detection is frequently confused with the sensitivity of the method. The sensitivity of an analytical method is the capability of the method to discriminate small differences in concentration or mass of the test analyte. In practical terms, sensitivity is the slope of the calibration curve that is obtained by plotting the response against the analyte concentration or mass.

FIGURE 11 – Limit of detection and limit of quantitation via signal-to-noise



SOURCE: Guideline (2005)

In chromatography, the detection limit is the injected amount that results in a peak with a height of at least two or three times the height the baseline noise level. Besides this signal-to-noise method, the ICH (GUIDELINE, 2005) describes three more methods:

1. Visual evaluation: The detection limit is determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level at which the analyte can be reliably detected.

2. The standard deviation of the response based on the standard deviation of the blank: Measurement of the magnitude of analytical background response is performed by analyzing an appropriate number of blank samples and calculating the standard deviation of these responses.

3. The standard deviation of the response based on the slope of the calibration curve: A specific calibration curve is studied using samples containing an analyte in the range of the limit of detection. The residual standard deviation of a regression line, or the standard deviation of y-intercepts of regression lines, may be used as the standard deviation. FIGURE 11 illustrates the graphical evaluations of LOD and LOQ via signal-to-noise.

TABLE 16 shows the methodology for quantitative detection limit measurements. Calculate the variance (s^2) and standard deviation (***s***) of the measures to replicate and calculate the LDM as follows:

$$LDM = t_{(n-1,1-\alpha)} \tag{4.6}$$

TABLE 16 – Determination of the limit of detection

Replicas	**Matrix,**	**Calculations**	**Observations**
≥ 7	Blank Samples	LD = $\bar{X}$ + ***t.s*** Where: $\bar{X}$ = the mean of the sample blank values; ***t*** is the abscissa of the Student distribution, dependent on the sample size and the degree of confidence, and ***s*** = standard deviation of the sample whites.	The mean and standard deviation of the sample whites are matrix dependent Valid only when the values of whites have a standard deviation other than zero

For example, in the case of analyzing 10 aliquots, will be 10-1 = 9 degrees of freedom from a blank matrix of the sample with the addition of the lowest acceptable concentration of the analyte. For these degrees of freedom, the unilateral t-value for 99% confidence is 2.8214. The LD will be equal to 2.8214 times the standard deviation.

The analytical method shall be specified and the LD for each analyte shall be expressed in the appropriate units, as recommended in the analytical method. The sample matrix used to determine the LD must be identified.

According to the ABNT NBR ISO/IEC 17025 in its guide DOQ-CGCRE-Rev. 05 – Ago 2016 the estimation based on the analytical curve from the simplified method the detection limit (LOD) can be calculated by the next equation:

$$LOD = \frac{3.3 * s}{b} \tag{4.7}$$

Where:

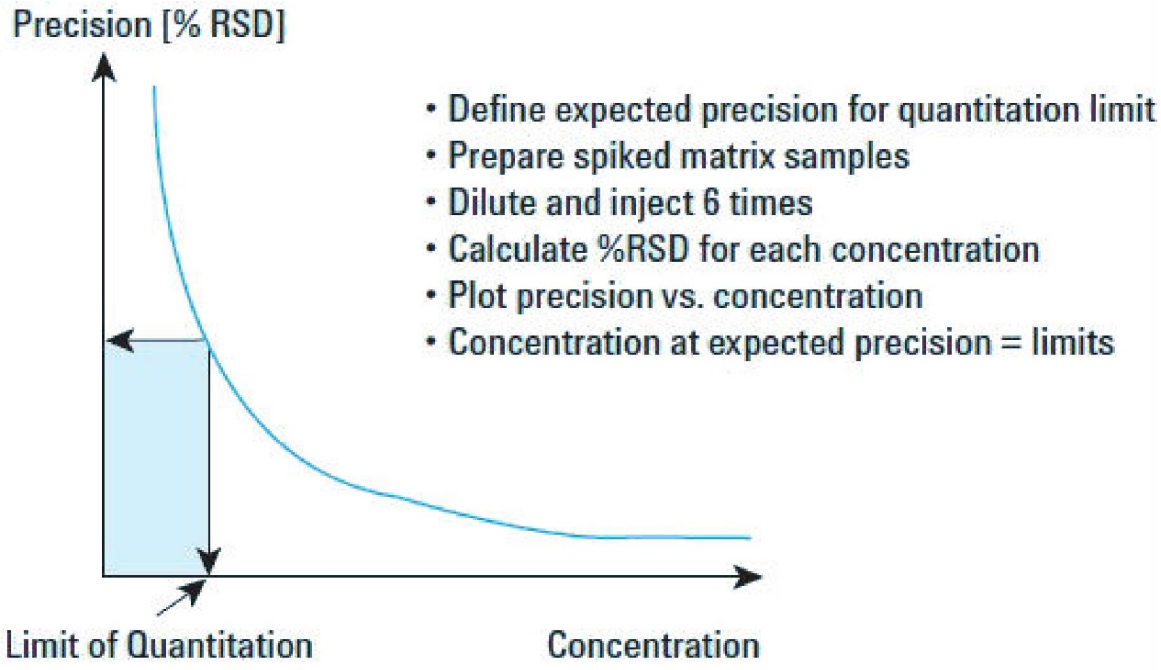
- ***s*** = standard deviation of white response
- **b** = slope (angular coefficient) of the analytical curve
- NOTE 1: This method provides better results at the trace level. At high concentrations, this method estimates LOD values above the real ones.
- NOTE 2: When the blank does not generate a signal, the standard deviation "***s***" of the lowest level of the analytical curve can be adopted.

- NOTE 3: The slope "**b**" can be estimated by an analytical curve of the analyte constructed in the evaluation of linearity.

4.1.6 Limit of quantitation or quantification (LOQ)

Guideline (2005) ICH defines the limit of quantification (LOQ) of an individual analytical procedure as the lowest amount of analyte in a sample, which can be quantitatively determined with suitable precision and accuracy. The quantification limit is a parameter of quantitative assays for low levels of compounds in sample matrices and is used particularly for the determination of impurities or degradation products. The quantification limit is generally determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level at which the analyte can be quantified with acceptable accuracy and precision. If the required precision of the method at the limit of quantification has been specified, 5 or 6 samples with decreasing amounts of the analyte are injected six times. The amounts range from the known LOD as determined above to 20 times the LOD.

FIGURE 12 – Limit of quantification based on selected precision



SOURCE: Guideline (2005)

The calculated relative standard deviation (RSD) percent of the precision of six repetitive injections is plotted against the analyte amount. The amount that corresponds to the previously defined required precision is equal to the limit of quantitation. It is important to use not only pure standards for this test but also spiked matrices that

closely represent the unknown samples. FIGURE 12 shows the required experimental steps and a typical graph.

The Limit of Quantification can be the concentration of the analyte corresponding to the value of the mean of the blank plus 5, 6 or 10 standard deviations. It is sometimes also called a "Determination Limit". In practice, it usually corresponds to the calibration standard with the lowest concentration (excluding blank). This limit, after being determined, should be tested to ascertain whether the accuracy and precision achieved are satisfactory. TABLE 17 presents a summary of the quantification limit determination method. The difference between the Detection and Quantification Limits is the order of magnitude of the associated uncertainties.

TABLE 17 – Quantification limit determination method

Nº of Replicas	**Matrix,**	**Calculations**
≥ 7	Blank Samples	LQ = $\bar{X}$ + 5***s*** LQ = $\bar{X}$ + 6***s*** LQ = $\bar{X}$ + 10***s*** Where: $\bar{X}$= mean of the sample blank values ***s*** = standard deviation of the sample whites
≥ 7	Blank Quantification Limits is the order of magnitude of the associated uncertainties. White with addition of varying concentrations of analyte, of the sample whites of the sample whites	Measure, once each, 7 independent replicates at each concentration level Calculate the standard deviation "***s***" of the analyte value for each concentration Graph the "***s***" versus concentration and assign a value to the LQ by inspection. Express the LQ as the lowest analyte concentration that can be determined with an acceptable level of confidence.

According to DOQ-CGCRE-Rev. 05 – Ago 2016 In the estimation based on the analytical curve from the simplified method the quantification limit (LOQ) can be calculated by next equation:

$$LOD = \frac{10 * s}{b} \tag{4.8}$$

Where:

- ***s*** = standard deviation of white response
- **b** = slope (angular coefficient) of the analytical curve

- NOTE 1: This method provides better results to trace level. At high concentrations, this method estimates LOQ values above the real ones.
- NOTE 2: When the blank does not generate a signal, the standard deviation "***s***" of the lowest level of the analytical curve can be adopted.
- NOTE 3: The slope "**b**" can be estimated by the analytical curve of the analyte constructed in the evaluation of linearity.

4.1.7 Accuracy

ICH defines the accuracy of an analytical procedure as the closeness of agreement between the true conventional value or accepted reference value and the amount found. Accuracy can also be described as the extent to which test results generated by the method and the true value agree. The true value for accuracy assessment can be obtained in several ways. One alternative is to compare the results of the method with results from an established reference method. This approach assumes that the uncertainty of the reference method is known. Secondly, accuracy can be assessed by analyzing a sample with known concentrations (for example, a control sample or certified reference material) and comparing the measured value with the true value as supplied with the material. If certified reference materials or control samples are not available, a blank sample matrix of interest can be spiked with a known concentration by weight or volume.

The concentration should cover the range of concern and should include concentrations close to the quantitation limit, one in the middle of the range and one at the high end of the calibration curve. Another approach is to use the critical decision value as the concentration point that must be the point of highest accuracy.

The ICH document on validation methodology recommends accuracy to be assessed using a minimum of nine determinations over a minimum of three concentration levels covering the specified range (for example, three concentrations with three replicates each). Accuracy should be reported as percent recovery by the assay of a known added amount of analyte in the sample or as the difference between the mean and the accepted true value, together with the confidence intervals. The accuracy expressed as the error percentage is calculated by:

$$\%ERROR = \frac{(X_{Exp.} - X_{True}) * 100\%}{X_{True}} \tag{4.9}$$

4.1.7.1 Certified Reference Materials (CRM)

Whenever possible, certified reference materials should be used in the validation process of a test method. An CRM has a concentration value, or another magnitude, for each parameter and associated uncertainty. It is very important, therefore, that the delivery of these CRM be carried out by recognized and reliable organizations (as for example NIST, LGC, etc.).

The correct use of CRM is its analysis to evaluate the performance of the laboratory. When the value obtained is not within the range of the acceptance region for the certified value, the laboratory should be searched for the causes of this deviation and seek to eliminate them. In the assessment of accuracy using reference material, the values obtained by the laboratory - mean and the standard deviation of a series of replicate assays - shall be compared with the certified values of the reference material. In this research the relative error will be used for this comparison.

4.1.7.2 Recovery

After extraction of the analyte from the matrix and injection into the analytical instrument, its recovery can be determined by comparing the response of the extract with the response of the reference material dissolved in a pure solvent. Because this accuracy assessment measures the effectiveness of sample preparation, care should be taken to mimic the actual sample preparation as closely as possible. If validated correctly, the recovery factor determined for different concentrations can be used to correct the final results.

The recovery of the analyte can be estimated by analyzing samples added with known quantities there of (spike). Samples may be added with the analyte in at least three different concentrations, for example, near the detection limit, near the maximum permissible concentration and at a concentration close to the average range of the method. The limitation of this procedure is that the added analyte is not necessarily in the same form as the one present in the sample. The presence of added analytes in a more easily detectable form and may lead to overly optimistic ratings of recovery. The recovery is calculated according to:

$$Recovery(\%) = \frac{(C_1 - C_2) * 100\%}{C_3} \tag{4.10}$$

Where:

- C_1 = concentration determined in the added sample,
- C_2 = concentration determined in the sample not added,

- C_3 = concentration added.

4.1.8 Precision

It indicates the degree of agreement between the results obtained for replicates of the same sample, applying the same experimental procedure under pre-set conditions. It is usually expressed regarding Standard Deviation (***s***). Another way of expressing accuracy is the relative standard deviation or coefficient of variation (CV), which is calculated as follows:

$$CV = \frac{S * 100\%}{\overline{X}} \tag{4.11}$$

4.1.8.1 Reproducibility

Reproducibility is defined by the USP as the degree of reproducibility of results obtained under a variety of conditions, such as different laboratories, analysts, instruments, environmental conditions, operators and materials. Ruggedness is a measure of the reproducibility of test results under normal, expected operational conditions from the laboratory to the laboratory and from analyst to analyst. Ruggedness is determined by the analysis of aliquots from homogeneous lots in different laboratories.

4.1.8.2 Repeatability

It is the degree of agreement between the results of successive measurements of the same measurand, carried out under the same conditions of measurement, called repeatability conditions, as follows:

- Same measurement procedure;
- Same observer;
- Same instrument used under the same conditions;
- Same location;
- Repetitions in a short time.

The repeatability can be expressed quantitatively in terms of the dispersion characteristic of the results and can be determined by the analysis of standards, reference material or white addition at various concentrations in the working range. We suggest 7 or more repetitions for the calculation of the standard deviation for each concentration, called the standard deviation of repeatability.

Repeatability limit - "r" from the Standard Deviation of the test results under repeatability condition is advisable to calculate the repeatability limit "r" which enables the analyst to decide whether the difference between duplicate analyzes of a sample, determined under repeatability conditions, is significant. The repeatability limit (r) is given by:

$$r = t_{\infty} * \sqrt{2} * S_r \tag{4.12}$$

Or at a level of significance of 95%:

$$r = 2,8 * S_r \tag{4.13}$$

Being S_r = Standard Deviation of repeatability associated with the results considered, if the laboratory obtains more than two results, the repeatability limit (r) is calculated according to ISO Standard 5725-6. It is advisable to evaluate the homoscedasticity (homogeneity of variables).

4.1.9 Robustness

ICH defines the robustness of an analytical procedure as a measure of its capacity to remain unaffected by small, but deliberate, variations in method parameters. It provides an indication of the procedure's reliability during normal usage.

Robustness tests examine the effect that operational parameters have on the analysis results. For the determination of a method's robustness, a number of method parameters, such as pH, flow rate, column temperature, injection volume, detection wavelength or mobile phase composition, are varied within a realistic range, and the quantitative influence of the variables is determined. If the influence of the parameter is within a previously specified tolerance, the parameter is said to be within the method's robustness range.

Obtaining data on these effects helps to assess whether a method needs to be revalidated when one or more parameters are changed, for example, to compensate for column performance over time. In the ICH document, it is recommended considering the evaluation of a method's robustness during the development phase, and any results that are critical for the method should be documented.

4.1.10 Uncertainties of measurement

Each measure implicitly implies an uncertainty, which is a parameter that characterizes the dispersion of values that can reasonably be attributed to the measured sample. The result of measurement includes the best estimate of the analyte value

and an estimate of the uncertainty about that value. The uncertainty is composed of contributions from various sources, some of them described by the respective input quantities. Some contributions are unavoidable due to the definition of the analyte itself, while others may depend on the measurement, method and procedure principle selected for measurement.

The results of a repeated measure affected by variations of influence varying randomly generally follow a normal distribution in good approximation. Also, the uncertainty indicated in the calibration certificates usually refers to a normal distribution. The way to express uncertainty as part of the measurement results is the confidence interval.

4.2 EXTRACTION PROCESSES

The Thermal Desorption (TD) equipment was then operated to place samples onto Peltier-based cold trap (CT), to thermally desorb analytes, and to transfer them into the GC for chromatographic separation and subsequent detection. The analytes were then separated on a Restek Rxi-624Sil-MS column (30 m x 0.32 mm x 1.8 μm) and detected by the MS detector. Ultra-pure He was used as a carrier gas at a constant flow rate of 2 mL·min^{-1}. The GC/Massa system was operated at flow rates of 30 (He) and 300 mL·min^{-1}.

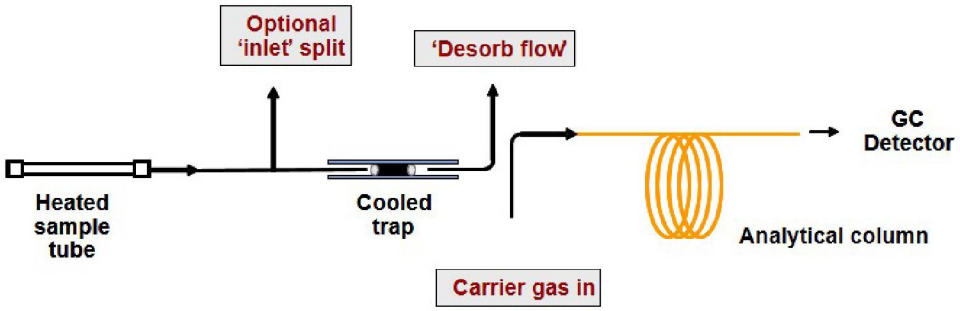
Thermal desorption is a technique that extracts volatiles from a nonvolatile matrix by heating the matrix/sample in a stream of inert gas. The extracted volatiles are subsequently refocused onto a cold trap from which they are transferred in a narrow band to a gas chromatographic column for analysis.

The sample is contained in a small-capped tube. The ATD takes a sample tube, uncaps it and seals it in the carrier stream. A leak test is automatically performed to ensure that the tube has been sealed correctly and to ensure that the rest of the system is leak-tight. The tube is then purged with carrier gas at ambient temperature to remove oxygen and moisture. The sample is subsequently heated with a flow of inert gas to extract the volatiles. The volatiles are concentrated on a low thermal mass, electrically cooled cold trap prior to transfer to the gas chromatographic column through a heated transfer line.

Heating the cold trap rapidly ensures that the analytes are transferred to the gas chromatograph quickly. This sample transfer method is fully compatible with high-resolution capillary chromatography.

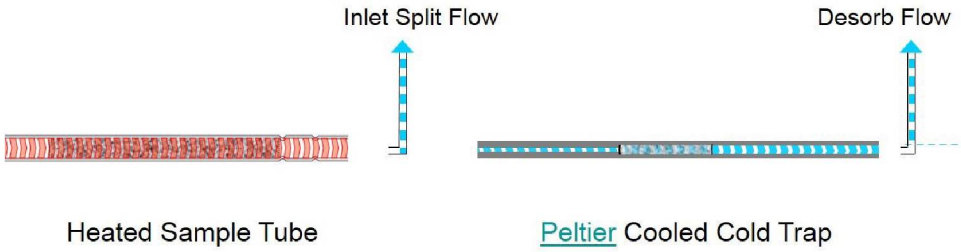
The diagram (FIGURE 13) below illustrates the first stage of the thermal desorption process. A flow of inert carrier gas is used to sweep adsorbed VOCs from the heated sample tube, to a low mass, electrically cooled cold trap. (FIGURE 14)

FIGURE 13 – First stage of the thermal desorption process



SOURCE: Perkin Elmer Co. (2011)

FIGURE 14 – Flow Direction in Primary Desorption



SOURCE: Perkin Elmer Co.(2011)

The cold trap re-focused the VOCs into a narrow band. In addition to a carrier gas pressure, it needs to send a Desorb Flow an optionally, and the Split Flow.

With the inlet split enabled the procedure followed was:

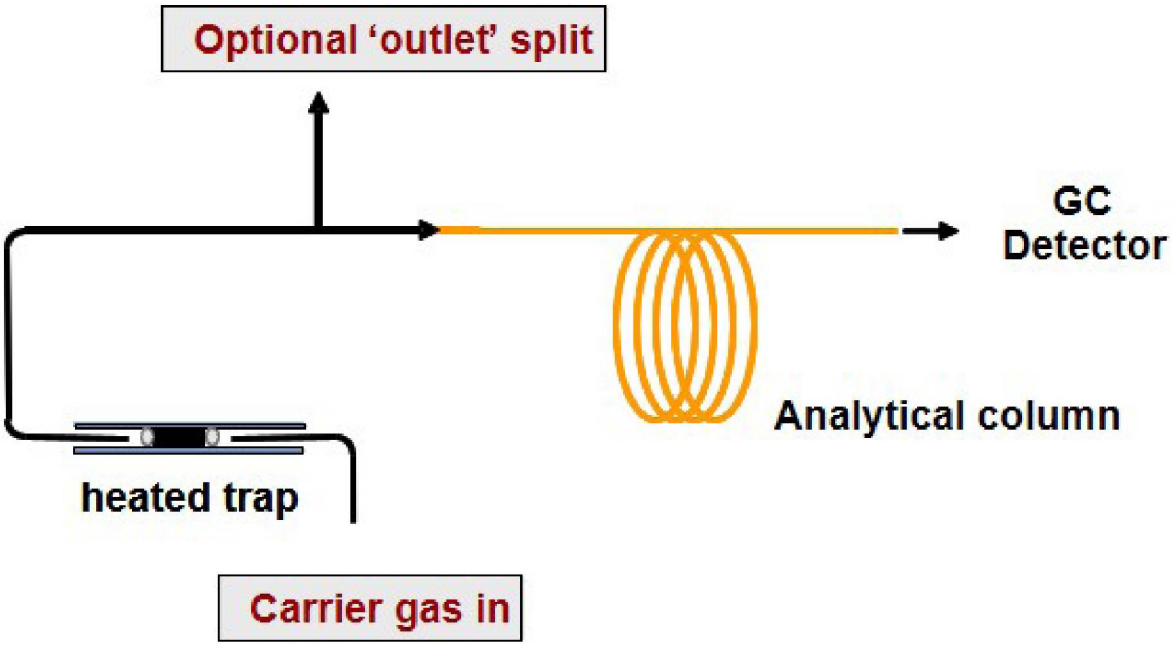
- The sample tube flow + Desorb flow + Inlet split flow;
- Only a portion of the sample is transferred to the cold trap, reducing sensitivity;
- The inlet split allows low trap (Desorb) flow to be combined with high tube flow;
- Absolute minimum trap flow during primary desorption should be 1.5 ml·min^{-1};
- Transferring only a portion of the sample to the trap avoids overloading issues.

The diagram (FIGURE 15) illustrates the final stage of the thermal desorption process.

The diagram (FIGURE 16) illustrates the direction of carrier gas flow through the Trap is reversed and the Trap is very rapidly heated to transfer the VOCs to the inlet of the analytical column.

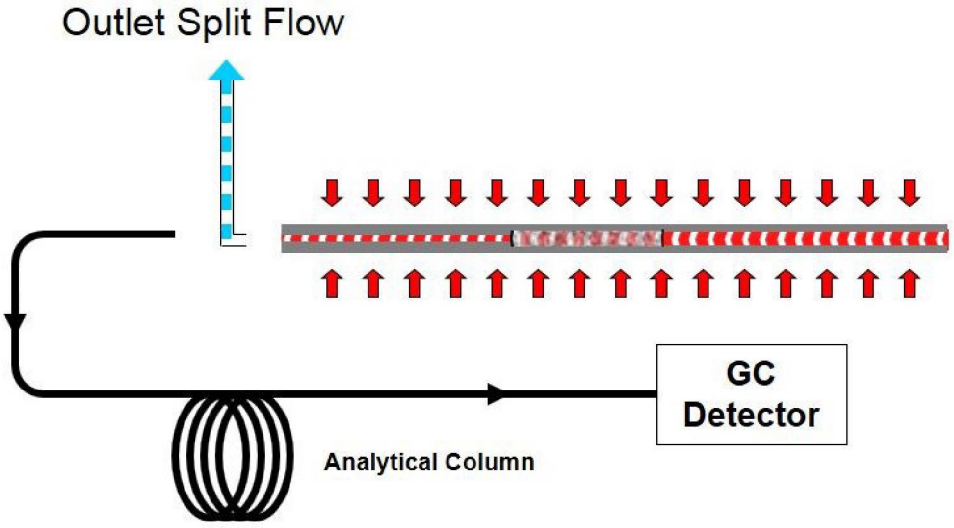
The advantages of using the two division states of the thermal separation system are:

FIGURE 15 – Secondary Stage of The Thermal Desorption Process



SOURCE: Perkin Elmer Co.(2011)

FIGURE 16 – Direction in Secondary Desorption



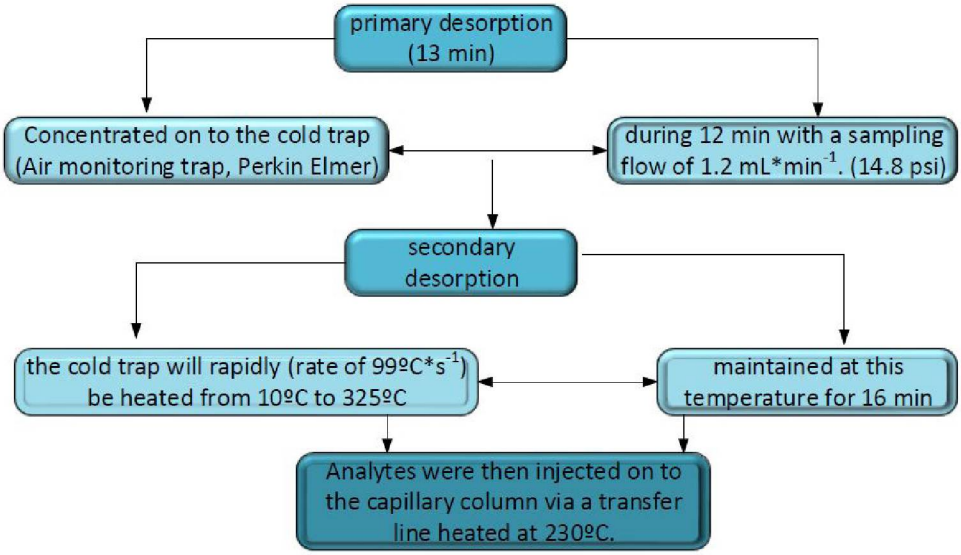
SOURCE: Perkin Elmer Co.(2011)

- The outlet split increase the flow through the Trap and aids the efficiency of the desorption process;
- Primary desorption transfers the VOCs from the bulky tube to the low mass cold trap;
- This trap is now heated at > 2000℃·min^{-1} to transfer the analytes to the column;
- As with the tube, the trap is backflushed (flow reversed) during the desorption;

- The outlet split increase the total trap flow and speeds up the trap desorption;

The following diagram (FIGURE 17) summarizes in a synthetic way the programming that was established to perform the thermal extraction in the ATD Turbomatrix 300 equipment.

FIGURE 17 – Programming thermal Desorption ATD 300 Turbomatrix



SOURCE: The Author

The parameters to be optimized during ATD method development are:

- Adsorbent selection;
- Desorption temperature;
- Desorption flow rate;
- Desorption time.

Ideally, we would like to achieve 100% desorption of the analytes from the tube. The injections/tube option can be used to easily test this result automatically.

4.3 ANALYSIS AND QUANTIFICATION OF BTEX BY GC – MS

Calibration curves were obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece (10 cm) of wide-bore (0.53 i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16”- 1/4”). The 1/4” Swagelock nut has to be equipped with a PTFE ferrule instead of the original steel one (use PTFE ferrules that come along with the Turbomatrix caps).

It introduced a blank cartridge in a Turbomatrix tube and fit the tube to the Swagelock nut. The injector was maintain at 200°C but do not heat the oven. Next, 1 μl of each calibration solution was injected under nitrogen flow (50 ml·min^{-1}) and let the system purge for 2 minutes. The cartridge was analyzed exactly as it was done with the sample. We prepared a complete set of calibration solutions by subsequent dilutions of 8, 4, 2, 1, 0.04, 0.02 and 0.01 μg·μL^{-1} of each compound.

Analysis of the standards and samples prepared in Methanol were performed in triplicate using a Perkin Elmer Clarus 680 GC gas chromatograph coupled to a mass spectrometer (Turbomass Clarus 600, Perkin Elmer). The capillary column used would be fused silica of the Restek having the reference Rxi-624Sil MS (30 m x 0.32 mm x 1.8 μm) 5% diphenyl phase and 95% dimethylpolysiloxane. The entrainment gas used was Helium at a constant flow rate of 1.4 ml·min^{-1} and a pressure pulse of 14.8 psi with a duration of 0.50 min. The volume injected was 1.0 μl in splitless mode. The oven temperature was programmed as follows:

- 1 minutes at 50°C, heated at the rate of 16°C·min^{-1} to 80°C and held for 1 min;
- Heated sequentially at a rate of 20°C·min^{-1} to 250°C and held for 1.5 minutes;
- Finally heated in sequence to 300°C at a rate of 10°C·min^{-1} and held for 5 minutes.

The temperatures of the injector, the GC-MS interface and the source (detector), were maintained at 300°C, 270°C and 260°C, respectively. These temperatures were taken based on the available literature review data and scientific notes from thermo desorption equipment suppliers.

4.3.1 Sampling rates

Taking into account the environmental temperature variations, the Passive Radiello sampling system provides sampling rate values at 298 K (25°C) and 1013 hPa are listed In TABLE 18. All of the values shown have been experimentally measured by the manufacturers of passive samplers Radiello. The supplier of the cartridges carried out tests of exposure to them up to the levels shown (in μg·m^{-3}·min) and sampling rates are guaranteed to be linear up to the limit values and for overall concentration of volatile organic compounds in the air not exceeding 2000 μg·m^{-3}.

TABLE 18 – Sampling rate by Radiello Passive Sampler Values at 25°(298 K)

Compounds	sampling rate ml·min^{-1}	exposure time (upper limit)	linear up to (μg·m^{-3}·min)	Uncertainty (2σ) (%)	LOD (μg·m^{-3})
benzene	27.80	7	410000	8.30	0.05
benzene	26.80	14	4100002	7.50	0.05
ethylbenzene	25.70	14	550000	9.10	0.01
toluene	30.00	14	550000	8.30	0.01
m-xylene	26.60	14	550000	11.30	0.01
o-xylene	24.60	14	550000	9.10	0.01
p-xylene	26.60	14	550000	11.30	0.01
Source: Sigma Aldrich \- Radiello, 2011					

4.3.2 Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

$$Q_{Ta} = Q_{298} * \left(\frac{T_a}{298 \quad K}\right)^{1.5} \tag{4.14}$$

Where:

- Q_{Ta} is the sampling rate at the temperature $\boldsymbol{T}_a$ and
- Q_{298} is the reference value at 298 K.

This produces a variation of ± 5% for 10°C variation (upwards or downwards) from 25°C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m·s^{-1}. The cartridges were always be protected from rain, however, upon reaching the laboratory a dry moisture extraction procedure was carried out, before being taken to the Thermal desorption system, to eliminate greater volumes of moisture from the cartridges exposed to environmental samples.

5 RESULTS AND DISCUSSION

The results and Discussion presented below is ordered sequentially according to the validation procedure of the analytical technique for the determination of BTEX in environmental air. The first step was the optimization of the parameters for the mass detector; for this purpose the analysis of a standard of average concentration was carried out and its analysis and reading was carried out in the GC-MS in the "full scan" mode, which allowed us to establish the time range in which each BTEX compounds was eluted from the standard of BTEX (Retention Time).

The time range in the full scan mode allowed to determine the time window in which the mass/charge ratio (m/z) should be maintained to allow only one of the BTEX ions generated to pass, which is called mode SIM (Single Ion Monitoring). When the SIM mode was defined in the GC-MS for each ion, we determined the absorption / desorption capacity of the Radiello cartridges used in the present study, which involved injecting standards into a GC equipped with a self-sampler (enrichment), used to minimize human errors during the injection process. This process was used to optimize the flow of the carrier gas and the time of flow maintenance in the auto sampler to allow greater efficiency in the transfer of mass from the vial (liquid) that contains the standard to the cartridge (gas).

Once the highest efficiency in the transfer of the standard was guaranteed, the separation conditions of each of the BTEXs in the gas chromatograph (GC-MS) were optimized. The optimized parameters were the heating rate of the furnace, carrier gas flows and the residence time of each temperature and flow condition.

Adjusting the conditions of GC-MS and the system of injection of standards, we optimized the parameters of the thermodesorption equipment, for which we programmed the conditions presented in the literature review. These conditions were heating temperatures rate and temperatures, gas flows in each stage, pressure conditions, and times in which the flow or temperatures are maintained. This procedure allowed us to establish the best thermal desorption conditions of the standards.

The final procedure consisted in the preparation of a series of dilutions from a certified primary standard of BTEX and the valuation of the linearity in the construction of the calibration curve, as well as the evaluation of the repeatability of each of the standards through the sequential injection of the same standard. The process was to establish if the peak generated in the chromatogram for the same standard varied in width or intensity. A variation in these conditions generated an adjustment of the conditions of the thermo desorption system (temperatures, heating rate, pressures,

flows).

The admissible linearity for the calibration curves was established for values of linear correlation coefficient (R^2) greater than 0.99 and the lowest relative standard deviation (RSD) calculated from the coefficient of variation (CV). Once this condition was met, we determined the validation parameters: working range, sensitivity, detection limit, quantification limit, precision, robustness. Each of the aforementioned stages is presented in detail as well as the results obtained for each of them.

5.1 OPTIMIZATION OF MASS DETECTOR (MS)

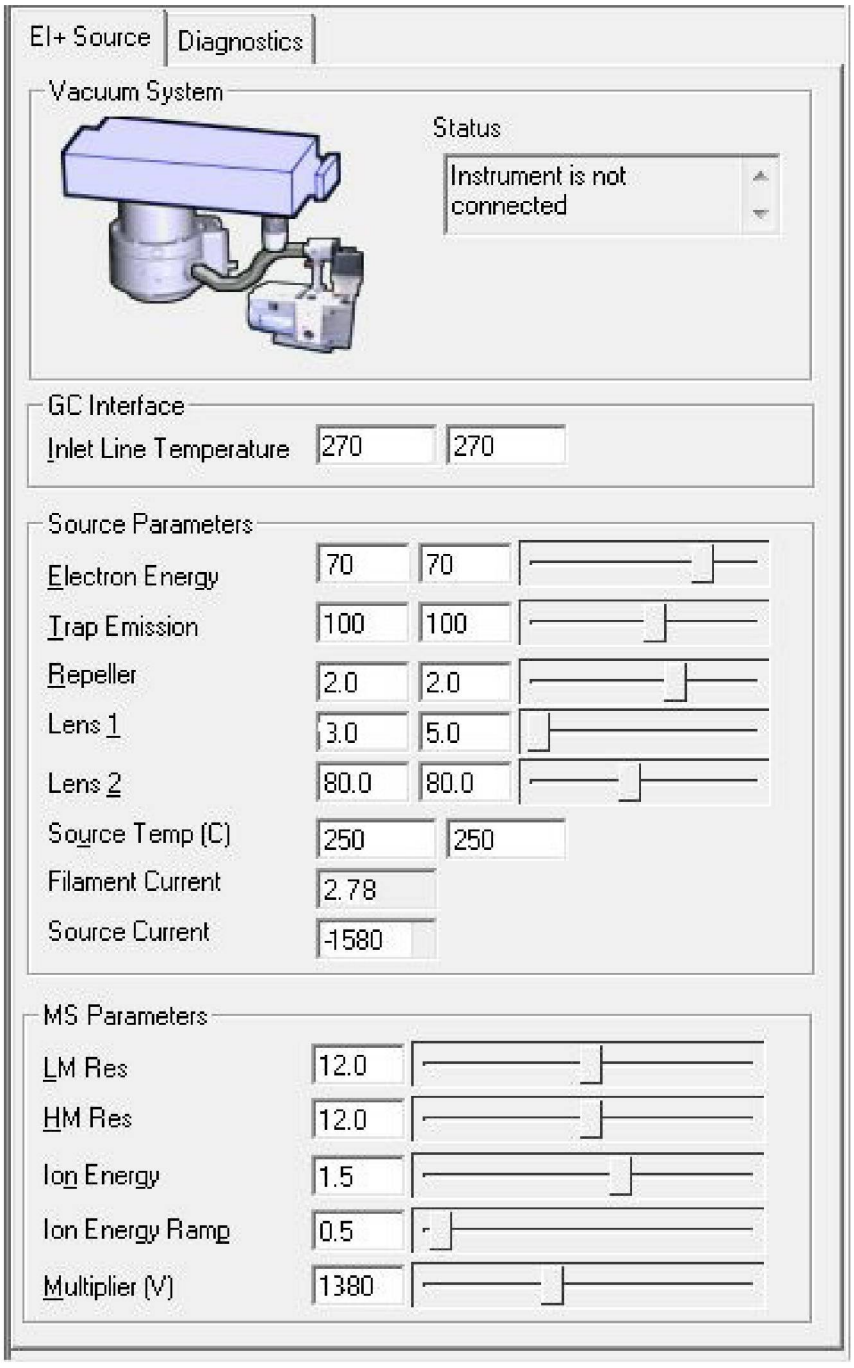
It was necessary to verify the adjustment conditions of the mass spectrometer and as well as to modify some of these parameters. The mass spectrometer was the UltraTuned automatically (Standard Tuning) from the Tune page. The TurboMass software of Perkin Elmer Clarus SQ 8T mass spectrometer allowed the mass spectrometer to automatically tune using the UltraTune with an ion source EI. The UltraTune allowed increasing the configuration of the adjustment parameters until the intensity, resolution and peak shape were optimized. During the development of the present investigation it was necessary to adjust the mass spectrometer twice: when the validation process was started and when it was necessary to perform a corrective maintenance to the same detector unit.

The objective of the Standard UltraTune is not only to give the "best" absolute harmony, but also, to provide good library search spectra with a reasonable sensitivity. High or low concentration range samples may require that we decrease or increase the electron multiplier voltage to obtain the best dynamic concentration range. In our study the multiplier voltage was maintained in 1380, to maintain the same conditions for both samples and standards. The Standard UltraTune determines the optimal configuration for Lens 1, Lens 2, Low Mass Resolution, High Mass Resolution, Ion Energy and the Repeller. The ion energy ramp should be set to 1.0 for a clean ion source and 3.0 for a dirty one. FIGURE 18 show the optimized conditions.

Reference Gas and Filament Control need to be adjusted during the Standard UltraTune process (FIGURE 18). The TurboMass software will assume control for switching the flow on and off. This software allows maintaining the file that records the tune parameters following a successful UltraTune. The following steps summarize the procedure for autotuning the mass spectrometer.

1. Display the Tune Page;
2. Start UltraTune. (Stock References Heptacosa - FC-43);
3. Setup UltraTune;

FIGURE 18 – Ultratune Mass Detector



SOURCE: Author. 2018

4. Accept the setup parameters;
5. Start tuning TurboMass;
6. Clear the UltraTune dialog box;
7. Start the mass calibration process;
8. Enter the Automatic Mass Calibration process;

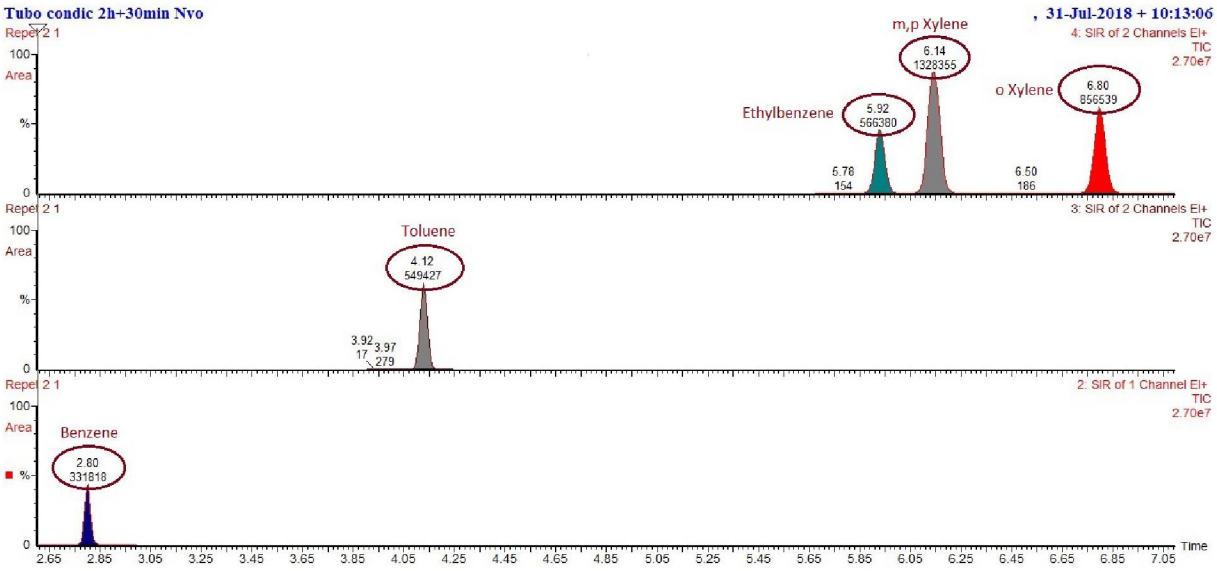
9. Start the mass calibration.

The retention times indicated in the standard chromatogram of FIGURE 19 are in the range established in the mass detector calibration procedure for each of the constituent compounds of the BTEX, indicated in TABLE 19. This procedure was performed through the SIM method of the mass spectrophotometer.

TABLE 19 – Retention time of compounds (BTEX) with Rxi 624Sil MS column

Compound	Primary Ion	Range	Secondary Ion	Time of Retention
Benzene	78	2.60-3.00	77	2.78
Toluene	91	4.04-4.15	92	4.09
Ethylbenzene	91	5.67-6.90	106	5.87
m,p-Xylene	91	5.67-6.90	106	6.09
o-Xylene	91	5.67-6.90	106	6.73

FIGURE 19 – Retention Time



SOURCE: Author. 2018

5.2 OPTIMIZATION TUBE CONDITIONING

It is essential that tubes are carefully conditioned before they are used for sample collection. Conditioning parameters should be more stringent than those to be used for subsequent analysis. Typically, tubes are conditioned at 10℃ below the maximum safe temperature of the least stable sorbent in the tube. The material used in the absorbent tubes Radiello is Carbograph 4, the characteristics of this material are described in TABLE 20.

TABLE 20 – Characteristics Carbograph 4

Sorbent type	Graphitised carbon black
Sorbent strength	Medium
Specific surface area	130 m^2/g
Approx. analyte volatility range	n-C4/5 to n-C12
Example analytes	Light hydrocarbons
Recommended conditioning temp.	Up to 380℃
Recommended desorption temp.	Up to 360℃
moisture absorption	Hydrophobic
artefacts	Minimal (<0.1 ng) artefacts (peaks on the blanck chromatogram - should be no more than 1 ng in Toluene equivalents for TenaxM and below 10 ng Toluene equivalents for other porous polymer sorbents)
Friable and compressible	CARE: Compressing these sorbents
Leads to high back	pressures and blocked tubes
Not recommended	for focusing traps
Repack tubes	after 200 thermal cycles

The equipment used was an international Markes TC-20 tube conditioner. The program of the conditioner was optimized to perform the cleaning of the cartridges in three stages: each stage lasted for one hour, with temperatures of 120℃, 240℃ and 380℃ and flows of 30 ml·min^{-1} (10 psi), 60 ml·min^{-1} (20 psi) and 90 ml·min^{-1} (30 psi) of Helium carrier gas, for the 1^{st}, 2^{nd} and 3^{rd} cycles, respectively.

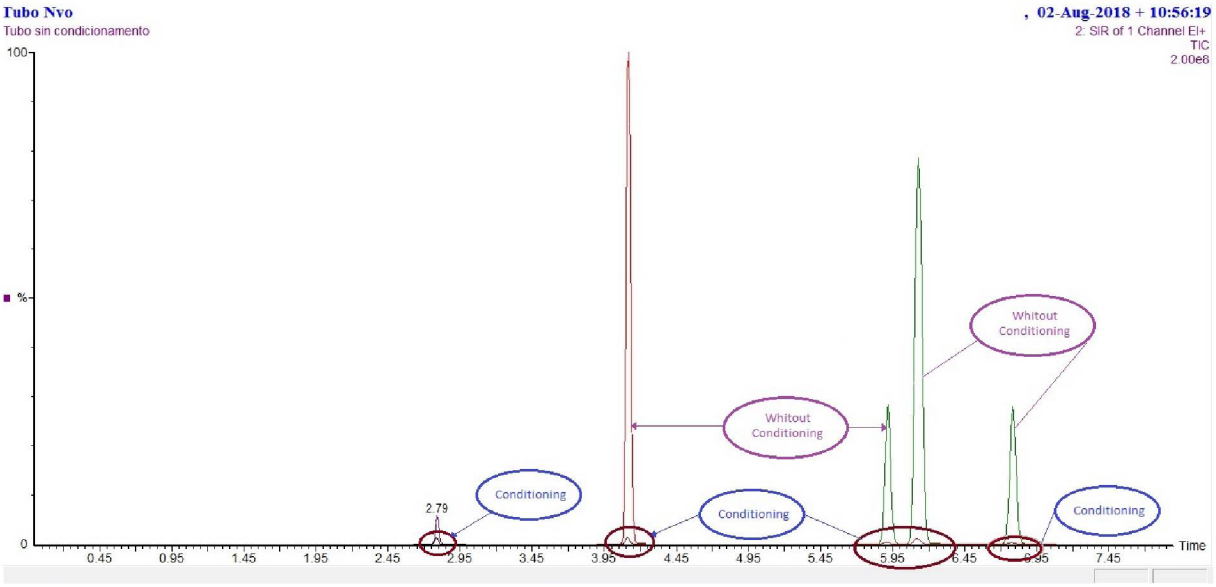
For tubes not freshly packed, i.e. those that have been used previously but need cleaning for future sampling, the final time and temperature given above will be sufficient. For the cleaning for example, used Carbograph4® tubes may be reconditioned at 335℃ for 30 min.

At the end of the conditioning program, the unit will start to cool down. We have to ensure that the flow of the carrier gas to the tubes is maintained until they have fully cooled back down to room temperature.

FIGURE 20 illustrates the peaks (Red and Green) resulting from the analysis of a new Radielo cartridge without conditioning. As noted in this Chromatogram, although

the cartridges are new, and the packaging is virtually sealed, they contain significant amounts of BTEX, which have been absorbed during the transport and storage of these cartridges. The small peaks marked in circles represent the baseline of the system, which was made with a cartridge conditioning. FIGURE 20 illustrates the significant difference between a cartridge conditioning and one without conditioning.

FIGURE 20 – Comparison chromatogram of a tube without conditioning and with conditioning



SOURCE: Author. 2018

5.3 OPTIMIZATION SPIKING

The calibration curves (10 calibration points) of the BTEX standards were made by adding 1 μl of the pre-prepared standard dilutions in the Carbograph 4 ™ absorber tubes. This process was carried out in a fully automated way, through the Perkin Elmer Clauros 680 automatic chromatograph injector; the calibration points chosen were the same in terms of the quantity injected for the line and tube calibrations. The Carbograph 4 ™ tubes were thermally conditioned before the Spiking stage (one hour at 120℃, one hour at 240℃ and one hour at 380℃). In order to limit any contamination of the system with the 1 ul of solvent deposited in the tube, especially the chromatogram profiles, at 50 ml·min^{-1} the He current passed through the adsorbent cartridge enriched for 2 minutes. The BTEX compounds were trapped by the adsorbent while much of the methanol evaporated. The evaluation of the advance volume showed that the general BTEX was trapped without losses. TABLE 21 summarizes the injection conditions of the standards in the adsorption cartridges.

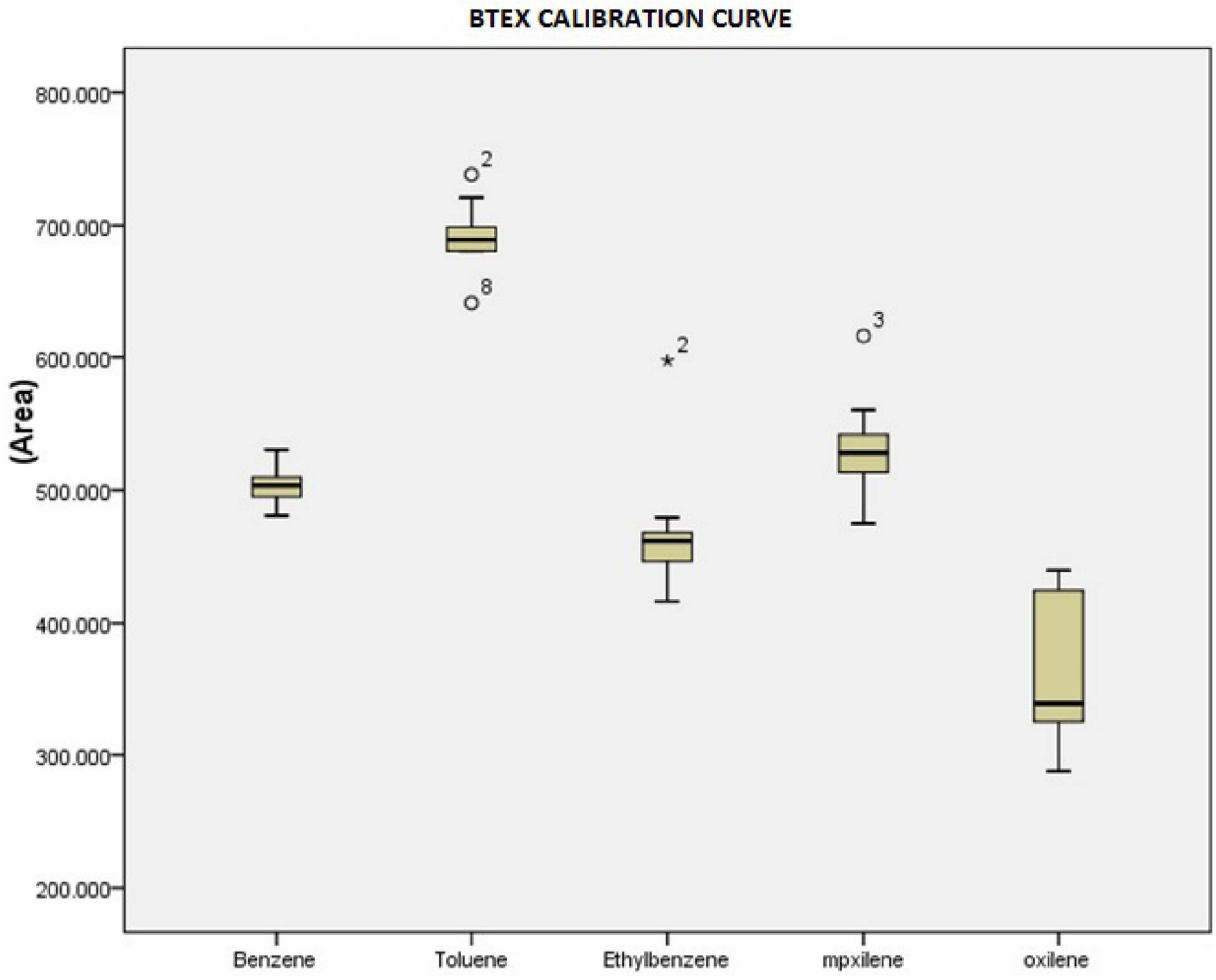
FIGURE 21 show the 9.85 μg·ml^{-1} point of calibration curve for the different compounds analyzed. This box plot highlights the very low dispersion of the Benzene

TABLE 21 – Optimization Injection stock

Step	**(ml·min^{-1})**	**Time (min)**	**Rate (ml·min^{-1})**
Star	50	2	100
2	2	1	END

and Toluene standards, as well as the high dispersion obtained for the o-Xylene pattern. It is necessary to indicate, also, that those injections of standards that presented a standard deviation equal to or greater than 2 were not taken into account to perform the calibration curve.

FIGURE 21 – Box Plot Stock 9.85 μg·ml^{-1}



SOURCE: Author. 2018

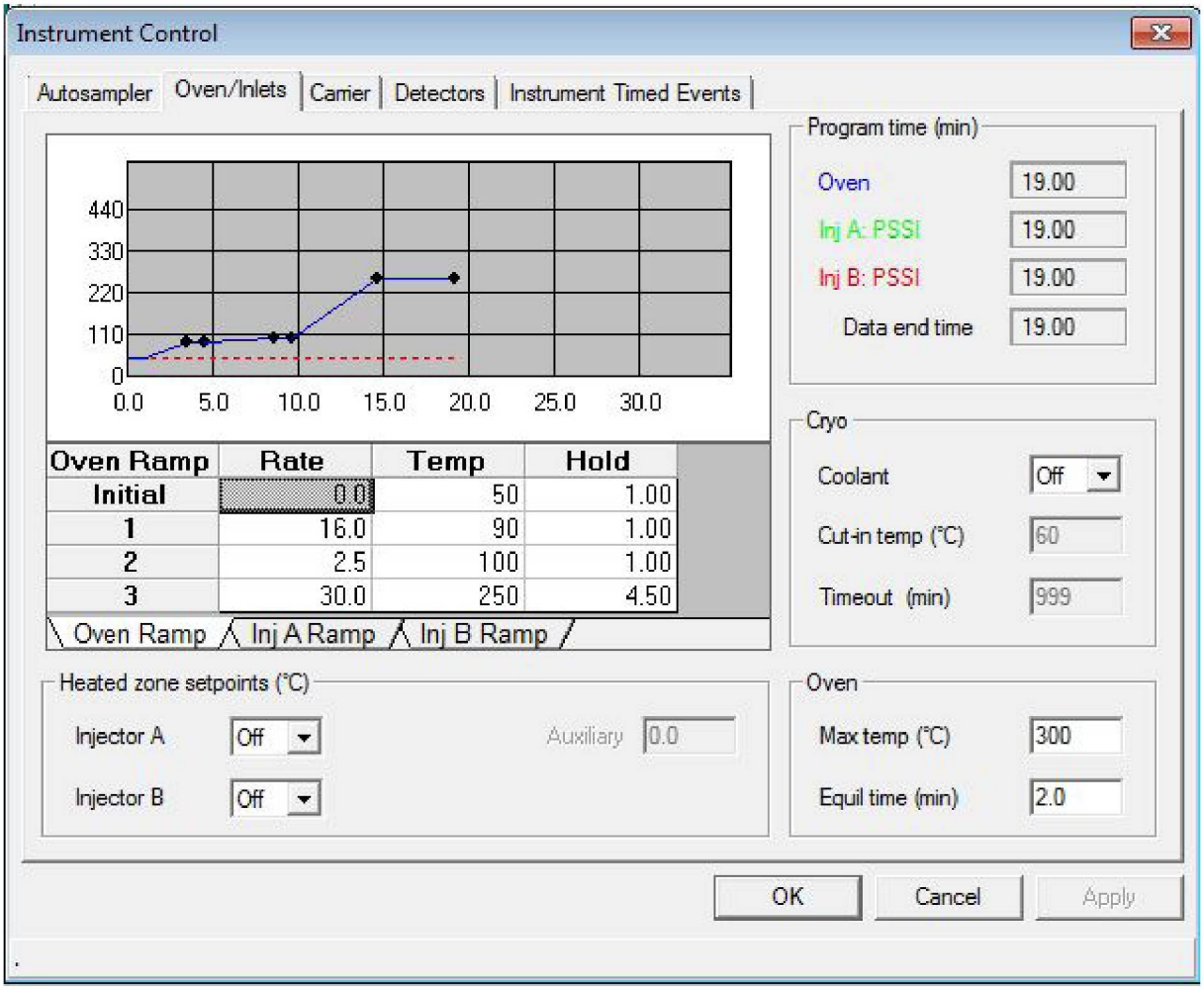
5.4 OPTIMIZATION OF CHROMATOGRAPH CONDITIONS

The objective of optimizing the conditions of the chromatograph is to allow the elution of each of the compounds retained in the column in an orderly, sequential and defined manner, seeking a clear and defined separation between each of the peaks of

the chromatogram resulted from the analysis of the sample. Because the BTEX are volatile compounds, we used a the 19-minute chromatograph program, with two basic objectives: to guarantee the elution of all the compounds and to improve the separation between the Xylenes.

The program starts at 55℃ because this is the temperature in which methanol, our solvent, evaporates, and therefore, we can start the quantification process. The final temperature of 250℃ has been established in order to elute heavier compounds and avoiding an interference in the readings, as well as any kind of interaction with the BTEX. FIGURE 22 presents the summary of the optimization conditions for the Clarus 680 chromatograph.

FIGURE 22 – GC-MS Conditions



SOURCE: Author. 2018

5.5 OPTIMIZATION OF THE THERMO DESORPTION (TD) SYSTEM

5.5.1 Temperatures

There are five temperature settings for the TD. The temperatures of the transfer line, the heat valve, the tube furnace and the secondary desorption temperatures of the cold trap (low and high). The heating rate for desorption secondary from trap was also established. During the whole process the precaution was taken not to enter a value of zero for any temperature parameter, as this would cause the related heater to be deactivated. For example, if you enter zero for the transfer line temperature, the transfer line heater will turn off and the transfer line will be at room temperature.

5.5.1.1 Transfer line temperature

The heated transfer line connects the ATD/TD to the gas chromatograph and consists of a heated stainless-steel tube containing the deactivated fused silica sample transfer line. A silicone foam tube forms the exterior insulation. The transfer line may reach between 50°C and 300°C. A chromatographic transfer line, which is either a length of deactivated fused silica, Silktec or the initial portion of the GC column, connects the ATD/TD to the GC.

The transfer line for the determination of BTEX was adjusted to 230°C in order to allow the complete transfer of BTEX from the Cold Trap system to the separation chromatographic column, Capillary Analytical Column is Directly connected to the TD.

5.5.1.2 Heated Valve Temperature

The heated valve is a 4-port rotary valve and is used to direct the carrier gas flow to the cold trap during the desorption process, or to isolate the cold trap during tube conditioning or the column during trap clean. The heated valve and its associated pneumatic connections may reach between 150°C and 300°C using the valve rotor supplied with the ATD/TD.

The temperature of the heated valve for BTEX determination was adjusted to 220°C to direct the flow of the carrier gas to the cold trap during the desorption process and to isolate the cold trap during the conditioning of the tube or column during cleaning of the trap.

5.5.1.3 Tube Oven Temperature

The tube oven consists of a thermostatted block that approximates the sample tube during primary desorption and heats it. The temperature, as well as the flow through the sampling tube, should be such as to ensure complete desorption of all analytes from

the sample. During the development of the validation process of the BTEX analytical technique with passive samplers, we tested different temperatures in the tube furnace, as well as different fluxes. We found from the tests carried out that the temperature in the tube furnace that allowed the total drag of the sample was 320℃.

5.5.1.4 Heat Rate

Once the volatiles were transferred from the sample tube, the trap was heated. The heating rate must be stablished to any value between 5, 20, 40 and 99-100℃/second (ballistic). The faster heating rates ensure that volatile compounds are transferred to the GC column in a narrow band. Lower rates provide slower heating so that the analysis of analytes can be thermally labile.

The second step of the heat rate is called secondary desorption. On this step the trap is heated to 325℃ at the selected rate. During the Secondary Desorption, the sample is released onto the GC column and the sample tube is conditioned by heating and venting through the Input Split flow control to prevent contaminants from entering the GC column. The analysis time for the GC method will determine the maximum condition time that can be set for the tube.

Many studies found that heating rates are relatively high, specially, for the BTEX determinations, for which heating rates of 99-100℃/s are usually used. No history of heating rates was found, so tests were not performed at different heating rates.

The temperature range that was maintained in the sample concentration system (cold trap) ranged from the lowest temperature (10℃) to the maximum temperature (325℃), whereby the desorption of the sample from the cold trap up to the column of the chromatograph showed a variation from 10℃ to 325℃ at a heating rate of 99-100℃/second.

The variation in the trap occurred in a time lapse of 3.15 s, which is necessary to ensure that the whole sample is desorbed from the concentration system and goes to the column of chromatographic analysis.

5.5.2 Timing

There are four timing parameters required to complete an ATD/TD method. The Purge time, the primary Desorption time, the Trap time and the Cycle time. The exact values of the compounds that we present here are based on their respective application. The ATD/TD timing parameters were also affected by the GC method.

5.5.2.1 Purge Time

Before the analysis, we performed the leakage test verification, in which air is purged from the tube prior to heating it for desorption. This is done to reduce the risk of adsorbent or analyte oxidation during desorption. The sample tube is purged with a carrier gas for the duration of the Purge Time. The minimum purge time is 1 minute in increments of 0.1 until 999.9.

The established flow conditions allowed the gas Helium to supply an inert atmosphere, favorable for the inhibition of oxidation processes, which was observed, due to the elution conditions of the peaks and their repeatability. We carried out the purging tests at 1, 2, 5 and 10 minutes. Taking into account the results of the peaks, and of course the minimization of the expenditure of ultra pure Helium gas, we decided to maintain a purge time of 1 minute.

5.5.2.2 Desorb Time (primary desorption)

The tube is then purged with a carrier gas at a room temperature to remove oxygen and moisture it. The sample is subsequently heated with a flow of inert gas to extract the volatiles. During the Desorb Flow Time, the tube oven was placed around the sample tube and it was heated with a continuous flow of carrier gas transferring the sample from the tube to the cold trap. The minimum desorb time was 1 minute. A flow of inert carrier gas (Helium) is used to sweep adsorbed VOCs from the heated sample tube to a cold trap that has low mass, and is electrically cooled.

The primary desorption occurs because of the action of two mechanisms acting simultaneously on the tube containing the sample: the heating temperature of the tube and the inert gas flow that allows the entrainment of the analytes to the trap. Defined the temperatures based on the boiling temperatures of the analytes under analysis, a series of tests were carried out with different flows, which guarantee the entrainment of the analytes once desorbed from the Radiello absorption system. The tests started with flows reported in the literature, for example Brown, Wright and Plant (1999) proposes a time for the primary desorption of 10 min, while Liaud et al. (2014) proposes 20 min. Due to the significant variation in the times referred to in the literature, it was necessary to perform a series of more significant tests, since variations of 1 minute were made, from a time of 10 minutes to 20 minutes. For each time, analyzes were carried out in triplicate, to determine the time in which the maximum efficiency for the analytical desorption of all the compounds of interest was reached.

We performed the primary desorption (desorption in the sample tube) at 8, 9, 10, 12, 14, 16, 18 and 20 minutes. Taking into account the evaluation criteria, peak height and residuality, the chromatograms of each of the samples ran in duplicate were

verified. We found that, for the times of 8, 9, 10, 12, 14 minutes, there was residuality in the second run of the sample, whereby we could not guarantee a complete removal of the analytes from the absorbent tube.

For the time 16, 18 and 20 minutes, complete removals of the analytes of interest (BTEX) were obtained, so we proceeded to evaluate which of them represented the best removal (in the primary desorption) and which of them allowed the lowest consumption of inert gas.

When performing the tests for these last flows, we found that the desorption time at 16.5 min was adequate enough to guarantee a 100% removal of the compounds of interest and an excellent definition of the peaks in the chromatogram as well as its maximum intensity and height.

5.5.2.3 Time Trap. desorption

In the software of the equipment ATD 300, when we press the Trap button, a Trap Timing dialog box appears. Temperature Hold Time specifies the length of time, during which the trap is held at its highest temperature for trap desorption. Typically, a period of 5 minutes is adequate (FIGURE 23).

FIGURE 23 – Trap Timing Popup

SOURCE: Perking Elmer 2009

Tests were performed with 8, 9, 10, 11, 12, 13, 14 minutes. Each of these tests was done in triplicate to verify mainly two criteria: the residuality and the height of the peak.

We performed the test twice for each tube in order to ensure that the analytes were completely extracted. The results showed the presence of fractions of the sample

in the tube after performing the first run, which allowed us to conclude that the desorption times of the trap at 8, 10, 11 minutes did not guarantee the complete extraction of the analytes from the concentration trap. This was clear because we found peaks of the analytes in the chromatogram that resulted from the second run of each tube.

For the tests at 12, 13 and 14 minutes, we found that in the second complete run of the sample there was no residuality in the tubes, as well as that the intensity of the peaks and the height of them remained practically constant. However, at 13 and 14 minutes, we could see that as time passed, there was a deformation of the peak of the analytes of higher molecular weight.

In conclusion, the results obtained for the time of desorption in the trap (secondary desorption) at 12 minutes were the most optimal in terms of residuality, intensity, height and peak shape. Therefore, we defined the time for the secondary desorption as 12 minutes.

5.5.2.4 Cycle time

The cycle time corresponds to the total analysis time, involving both the extraction stage (primary and secondary desorption) and the chromatographic analysis stage. Taking this into account, the total time will be the sum of the time of the primary desorption (12 min.) plus the time of secondary desorption (16.5 min) and the time of separation and analysis in the chromatograph. However, it is necessary to take into account that in each desorption a purge occurs which is necessary to eliminate impurities from both the tube and the sample concentration system. It is also necessary to take into account that once the secondary desorption (desorption of the trap) is the samples begin to the taken into the chromatograph, and therefore the chromatographic analysis is initiated, which means the a reason for which secondary desorption occurs simultaneously with the chromatographic analysis.

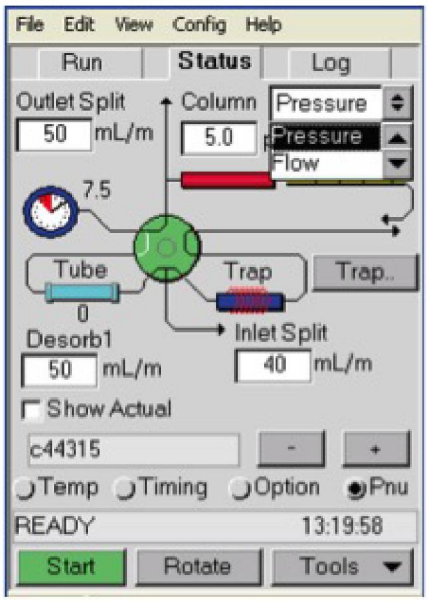
The analysis time in the chromatograph is 19 min. (see FIGURE 24), the purge times of the first and the second desorption are respectively one and two minutes, plus the time of the primary desorption itself which is 12 min, for which the total analysis time for each sample is 34 min. It is also necessary to mention that once the total analysis stage has finished, the thermo-desorption equipment must return to the low temperature (10 °C) (see section 5.5.1.4) to avoid losses of the absorption tube that contains the sample. In cooling process, the ATD 300 equipment usually takes approximately 10 minutes; this condition means that the actual injection time of one sample with respect to the next is 45 min. However, the cycle time that was programmed in the thermo-desorption equipment was 34 minutes, because this time interval involves the optimized time of primary desorption, and the optimized, but simultaneous time of secondary desorption and chromatographic analysis.

TurboMatrix 300 TD Single-tube model, incorporating programmable pneumatic control (PPC), upgradeable to the automated version, Supports pressure, flow and velocity control of the carrier gas through the GC column. It also includes a separate trapclean-and-test function which saves time and protects the GC column and detector.

5.5.3 Flow control: Programmable pneumatic control (PPC)

The Pneumatic Control System of the Perkin Elmer ATD 300 equipment used allows to select the flow control system (Desorb Flow Rate) in the column, by means of the option of flow or pressure control, as well as to select if the sample will be divided in the input of the sampling tube (inlet split), or after the concentration of the sample in the trap (outlet split), it also allows to observe the current tube number and the number of injections of this tube (FIGURE 24).

FIGURE 24 – Pneumatics Tab Column Dropdown TurboMatrix 300 TD



SOURCE: Perking Elmer 2009

5.5.3.1 Desorb Flow Rate

To establish the desorption flow relationship, it was necessary to take into account the variations in the flow that can occur in the system due to changes in the temperature conditions of each of the components of the system. The temperature passing from 10℃ to 325℃ (first desorption) generates a drastic expansion of the gases, a higher pressure and therefore a drastic flow variation. In the same way, in the concentration system of the sample (trap), an equivalent temperature variation occurs. It is necessary to remember that once the secondary desorption that occurs in the trap begins, the sample will begin to be injected in the column of the chromatograph as well in order to maintain conditions as stable as possible once the sample arrives

at the chromatograph, so it was necessary to select the option 'pressure' instead of 'flow', so that when the equipment automatically changes, the temperature will also adjust the pressure of the system, to keep it constant, during each of the stages of the thermo-desorption process.

Again, a series of tests were carried out to establish which pressure was the best condition for desorption; the pressure variations were 8, 9, 10, 12, 14, 16, 18 psi (FIGURE 23). Each of these pressure values were evaluated with a standard of 2 μg·ml^{-1}. The results allowed to establish that, for the pressures of 8, 9, 10, 12 psi, there were significant decreases in the heights of the peaks, as well as their deformation. For the pressures of 16 and 18 psi, the union of peaks was presented in the chromatogram, for example, the peaks of xylenes eluded completely bound, thus not allowing adequate separation of the compounds under study.

For the pressure of 14 psi, a series of tests were carried out to optimize the height and shape of the peak, finding that the pressure of 14.8 psi allowed to obtain the best conditions of peak height, shape and peak separation, therefore, this was the work pressure established for the column.

5.5.3.2 Inlet and outlet split

When the carrier flow is set so is the flow for the desorption system which includes purging the sample tube, primary and secondary desorption, inlet and outlet split flows and the GC column flow rate. Relatively high flow rates (20 to 100 ml·min^{-1}) are required for purging and desorption. Substantially lower flow rates (1 to 5 ml·min^{-1}) are required for capillary column chromatography. The multiple splitter allows you to set the required desorption rates and provides the lower column flow rates required by the GC. The Outlet Split flow was set separately using the Outlet Split needle valve. The carrier pressure was set first. Then the desorb and inlet split flows were set. Lastly, the outlet split flow rate was adjust, was powered up the instrument before setting the carrier pressure and the various flow rates.

5.5.3.3 Two Stage Desorption

This is the mode used to perform most of the analyses. Primary Desorb takes place after the sample tube leak is tested and purged of air. It was heated for a set period while a stream of inert gas sweeps the volatiles contained in the tube onto the cold trap where they are re-concentrated. The cold trap contains an adsorbent material to trap the volatile sample components. At the end of this period, the Secondary Desorb takes place. The trap was heated rapidly to release the volatiles onto the GC column.

The criterion for the determination of the division of the inflow is basically the minimization of the moisture content that leaves the tube that contains the sample and

reaches the sample concentration system (Cold Trap.), based on the consideration that the validation of the sampling will be carried out at the Port of Paranaguá, because it is close to large bodies of water it will probably contain significant amounts of moisture, which is why we only took into account the Split option at the entrance of the tube, and also considered flows that allow high divisions.

The starting point to consider the division flow at the entrance was the one proposed by the manufacturer of the Radiello passive sampling tubes in its application note E1 of 2006 for the determination of Volatile Organic Compounds (VOCs), in which rates are proposed of split of 90 ml·min^{-1}, we also took into account the application notes of the manufacturer of the analysis equipment (Perkin Elmer, 2015) for the determination of VOCs by the EPA method TO-17, where rates are recommended of split of 18 ml·min^{-1}. From these considerations, different sample split tests were started at the entrance, the rates evaluated were 18, 20, 30, 40, 50, 60 and 90 ml·min^{-1}.

The rates of 30, 40, 50, 60, 90 ml·min^{-1} imply higher divisions, that is, lower amounts injected into the chromatographic column, so, for example, percentages were obtained for the proposed input split of 3.44, 4.09, 4.36, 4.67, 5.03 and 5.45 % respectively, the procedure of this calculation is based on the following equation:

$$\% \quad Injected = \frac{FlowInColum * FlowDesorption}{[(SpliOut + \ FlowInColum) + (FlowDesorption + SplitIn)]} \tag{5.1}$$

For the validation conditions that were established for the TurboMatrix Series 300 TD equipment, the calculation procedure was:

$$\%Injected = \frac{(1.4 * 100)ml * min^{-1}}{\left[(20 + 1.4)\, ml * min^{-1} + (100 + 20)\, ml * min^{-1}\right]} * 100\% = 5.45\% \tag{5.2}$$

This volume is considered adequate because of two basic criteria, one that if the sample contains moisture, as is to be expected for the environmental conditions of Paranaguá, the low percentage injected will allow the elimination of a significant portion of this humidity, and two that the low proportion injected will also allow injecting lower concentrations in the column of the analytes under study (BTEX). However, of the Cold trap system allows to concentrate the sample in a significant way.

The previously injected percentage calculations were made starting from an output split flow of 20 ml·min^{-1} constant, for the different proposed input split values. In the same way, we proceeded to adjust the output division values to optimize this parameter as well, taking as reference the values proposed by the application notes of the Radiello passive sampler of 2006, where an output split value of 30 ml·min^{-1} is proposed, in addition to the application notes of the equipment manufacturer (Perkin

Elmer in 2015), where split value is proposed at the output of 18 ml·min^{-1}. Therefore, output split values of 15, 18, 20, 25, 30 ml·min^{-1} were evaluated, for which split percentages of 7.11, 6.01, 5.45, 4.42 and 3.72% were obtained, respectively. The previous values were obtained keeping the input split flow constantly at 20 ml·min^{-1}.

For the proposed split-output values, we found that the best intensity, peak height and the shape of the peak was the output split flow of 20 ml·min^{-1}. Status conditions dialog box consists of four views: Temperature, Timing, Options and PNU. It is possible to view the Actual values as they are on the ATD/TD or view the Set Points. If it possible to view the Actual values, the parameters that have reached their set point are displayed in black, those that are still changing are highlighted in yellow and displayed in red.

5.6 PREPARATION OF STANDARDS

Only one vial was used for each standard. The vials containing the standard were never reused. The field samples do not require any type of treatment with glass, because they are extracted directly from the thermo-desorption equipment.

Samples and standards were prepared on calibrated and verified analytical scale, with a room temperature of 20℃. The scale used to prepare the standards had a correction of 0.054 mg (standard mass of 0.2 g) and the standards of concentrations had a combined uncertainty ranging from 0.00019 to 0.00021 μg·ml^{-1}. The scale used to prepare the samples had a correction of 0.09 mg (standard mass of 50 g) and an uncertainty ranging from 0.067 to 0.165 μg·ml^{-1}. The uncertainties of the equipment were taken from the calibration certificates of scale.

The results illustrated in TABLE 22 allow us to observe how the secondary standard of 100 μg·ml^{-1} was obtained. As well as the weighting of the standards of 10 and 2 μg·ml^{-1}, performed in triplicate, initially weighting the empty vial, with the standard and with the solvent. The results expressed as C2 correspond to the concentration after the dilution process, while C1 represents the concentration of the initial standard solution, as well as V1 represents the volume taken from the initial standard solution and V2 corresponds to the final volume to which the final standard solution was taken after the dilution process.

The analysis was performed in Single Ion Monitoring (SIM). This analysis mode of the mass spectrometer performs the monitoring of only one ion or mass during a certain time interval. The spectrometer used in the analysis makes it possible to carry out a scan of the masses (Scan mode), and we are able to identify possible interferences. The solvent used to determine contaminants was also analyzed. All the glassware used in the preparation of standards was new glassware.

TABLE 22 – Preparation of Standard

V1 (ml)	Vacuo(g)	Stock(g)	Solvent(g)	C1 (μg·ml^{-1})	V2(ml)	C2 (μg·ml^{-1})
0.0764	2.7261	2.7866	4.0022	2029	1.6123	96.1950
0.0766	2.7260	2.7866	4.0021	2029	1.6123	96.3540
0.0766	2.7259	2.7865	4.0021	2029	1.6124	96.3465
0.1588	2.7229	2.8486	3.9513	96.1950	1.5520	9.8435
0.1587	2.7230	2.8486	3.9513	96.2985	1.5519	9.8470
0.1588	2.7230	2.8487	3.9513	96.2985	1.5519	9.8549
0.0335	2.7201	2.7466	3.9809	93.8819	1.5929	1.9732
0.0336	2.7200	2.7466	3.9810	93.8819	1.5932	1.9804
0.0334	2.7202	2.7466	3.9810	93.8819	1.5929	1.9658

5.7 CURVE CALIBRATION

From the areas of peaks obtained for each standard of the calibration curve, the calculation of standard deviation was carried out, and with this value, as indicated in 4.1.8 and in equation 4.11, the coefficient of variation was calculated of which is the precision indicator. TABLE 23 illustrates areas obtained for some of the Benzene standards that were prepared and analyzed, such as the results of the calculations obtained for the standard deviation and the coefficient of variation.

FIGURE 25 and FIGURE 26 show the peaks of the chromatograms obtained for each standard. In these chromatograms, peaks can be observed for the same compound at different intensities. This corresponds to the different concentrations injected for each of the calibration ranges obtained. TABLE 22 and TABLE 23 show each one of the obtained values is presented, both for the preparation of the standards, for the realization of the calibration curves, and for the same calibration curves.

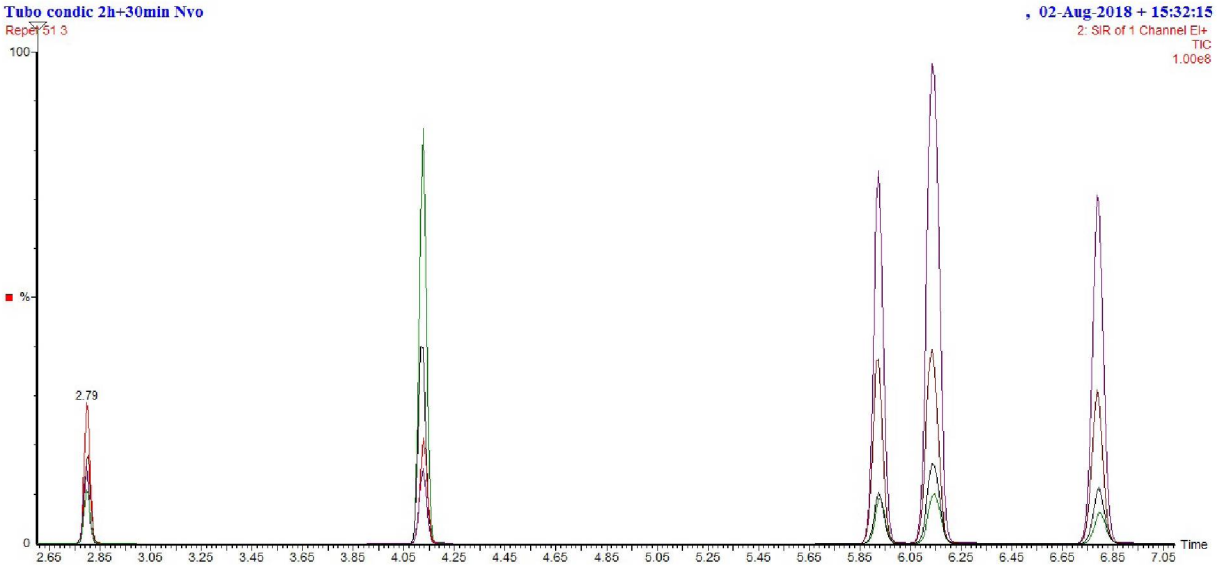
5.8 WORKING RANGE, LINEARITY AND SENSITIVITY OF BTEX

The results of working range, linearity and sensitivity were obtained by adding of standard of known concentration, which were prepared from a Supelco certified stock of 2000 μg·ml^{-1}, for which an uncertainty of 12.9% was reported for Benzene, 2.0% for Toluene and Ethylbenzene, 1.0% for m-xylene and p-xylene and 4.0% for o-xylene. From the injection of these standards the development of two calibration curves, one called low range (1.00 to 80.00 μg·ml^{-1}) and one called high range (80.00 to 400.00 μg·ml^{-1}) was determined, TABLE 24, TABLE 25 and TABLE 26 illustrate the working range, the values of the linear correlation coefficient (R^2) and sensitivity (slope of the linear regression) that allows establishing the linearity of each of the calibration points.

TABLE 23 – Calibration curve data from the peak areas for BTEX

C2 (μg·ml^{-1})	Stock (μg·ml^{-1})	Área Benzene	Average	SD	CV
96.1950	96.2985	3788005	3748516	60992	1.63
96.3540		3779274			
96.3465		3678269			
9.8435	9.8485	506574	496490	10079	2.03
9.8470		496480			
9.8549		486416			
1.9732	1.9731	384218	381137	18909	4.96
1.9804		360876			
1.9658		398316			
29.1283	29.1283	665893	637119	23046	3.42
29.1203		654553			
29.1363		698912			
51.6251	51.6199	900788	891260	10404	1.17
51.6243		892833			
51.6103		880160			

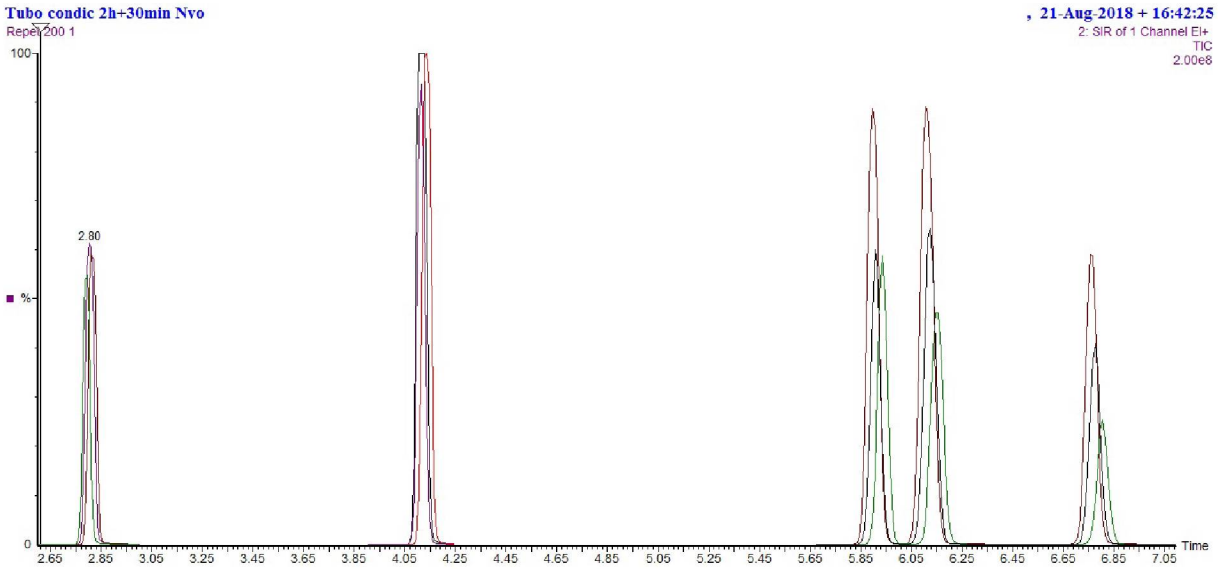
FIGURE 25 – Stock Low Range



SOURCE: Author. 2018

The calibration curves derived from the analysis for all 6 BTEX have globally denoted a good linearity for analytical method. However, the linearity was biased for low concentration constraining us to elaborate two calibration curves for analytical instrument, which implies changes in the working range: one for low range (FIGURE 27

FIGURE 26 – Stock High Range



SOURCE: Author. 2018

Curves a) to e)) injected quantities between 0 and 80 ng corresponding to 0-80 μg·ml^{-1} range and one for higher range (FIGURE 28 Curves f) to j)) injected quantities 80 to 400 ng corresponding to 80-400 μg·ml^{-1}. Despite, the correlation coefficients R^2 ranged from 0.9905 to 0.9988 (TABLE 26) for ATD-GC-MS in the SIM mode calibration.

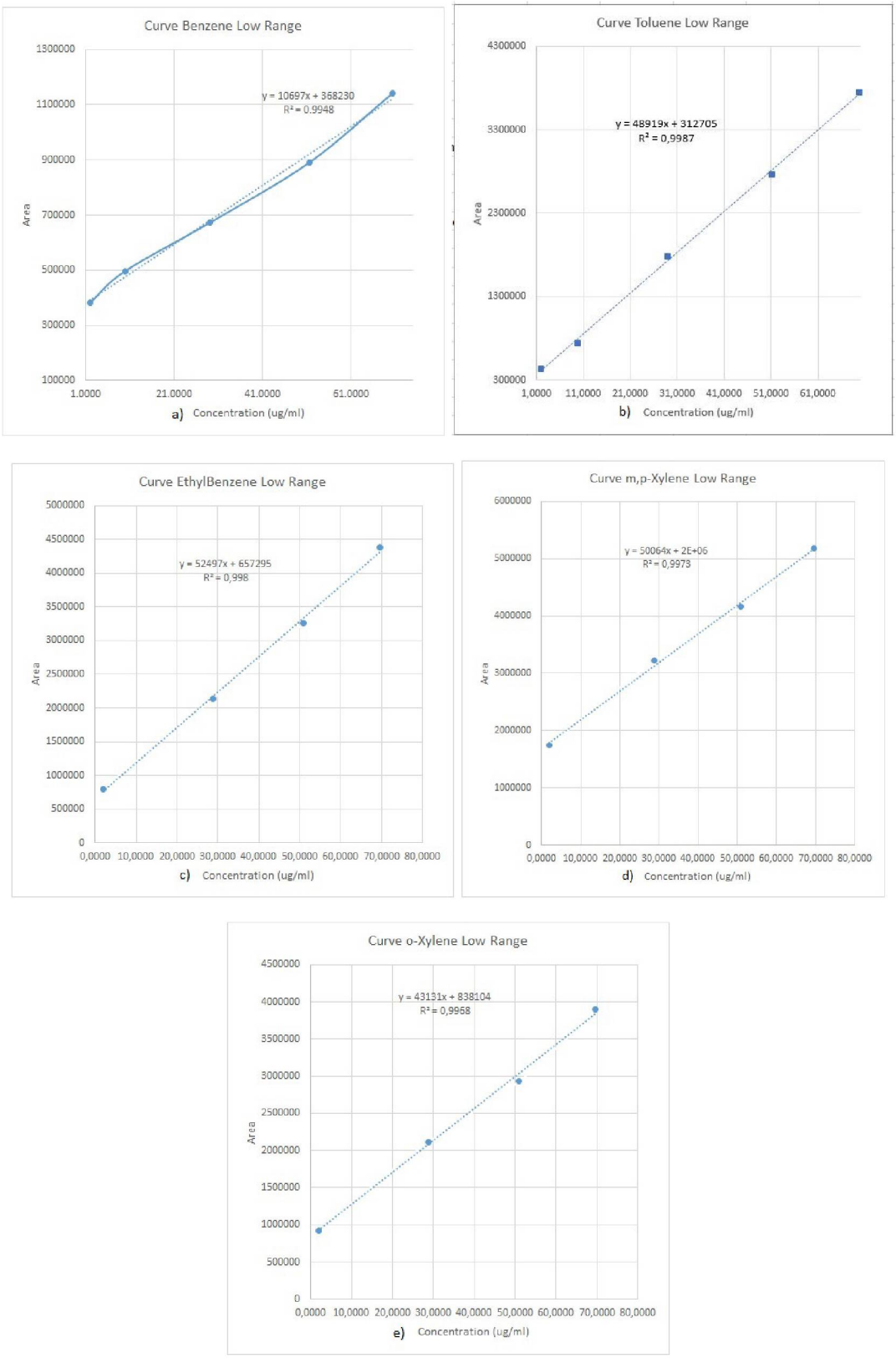
The values presented in TABLE 24 are in the mass work range of the values presented in TABLE 7: 0 to 400 ng of BTEX. The values reported by Liaud et al. (2014) show sensitivities widely higher than those obtained in the present study; however, the sensitivities we obtained for the BTEX, illustrated in TABLE 24 and TABLE 25, show higher sensitivities than those obtained in Pandey and K.-H. Kim (2009a), Cavalcante et al. (2010), Du et al. (2013), Pandey and K.-H. Kim (2009b), and Y.-H. Kim and K.-H. Kim (2012).

Taking into account that the comparisons are made for the calibration curve, the values reported in the present study correspond to μg·ml^{-1}, and were converted to mass after we multiplied the concentration by the final volume of preparation (C2): For many of the literature related studies, the validation data are expressed in μg·m^{-3} because the validation of the field sampling stage need to be performed. In the present study, only the data of the validation process in the laboratory are presented.

TABLE 24 – Working Range BTEX

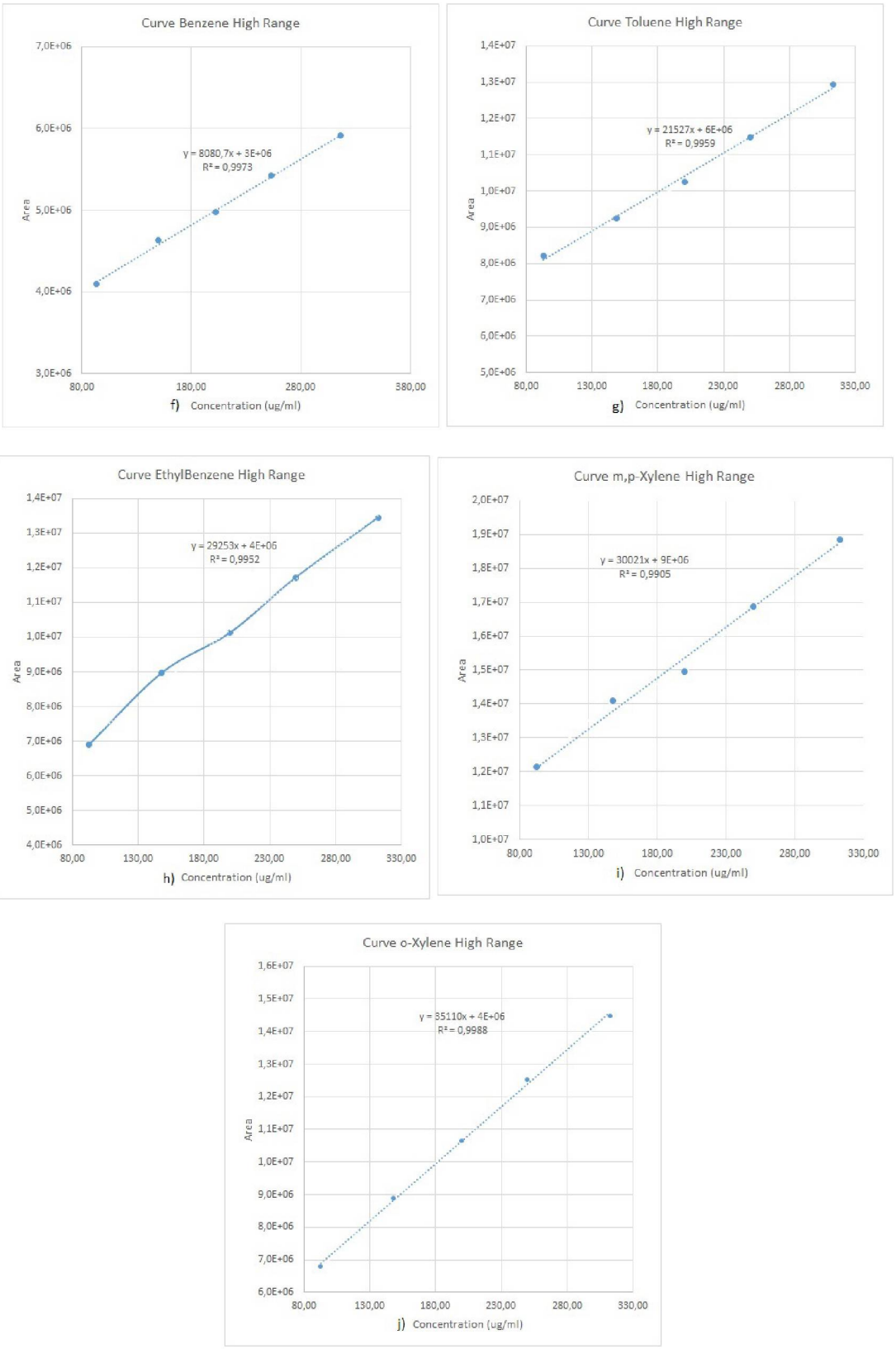
Range	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
0-80 ng	10697x	48919x	52497x	50064x	43131x
80-350 ng	8080x	21527x	29523x	30021x	35110x

FIGURE 27 – Curve Calibration Low Range BTEX



Source: Author, 2018

FIGURE 28 – Curve Calibration High Range BTEX



Source: Author, 2018

TABLE 25 – Sensitivity and linear coefficient (R^2) for BTEX Low Range by TD/GC-MS

BTEX	Sensitivity	(R^2)
Benzene	10697	0.9948
Toluene	48919	0.9987
Ethylbenzene	52497	0.9980
m,p - Xylene	50064	0.9973
o - Xylene	43131	0.9968

TABLE 26 – Sensitivity and linear coefficient (R^2) for BTEX High Range by TD/GC-MS

BTEX	Sensitivity	(R^2)
Benzene	8080	0.9976
Toluene	21527	0.9959
Ethylbenzene	29523	0.9952
m,p - Xylene	30021	0.9905
o - Xylene	35110	0.9988

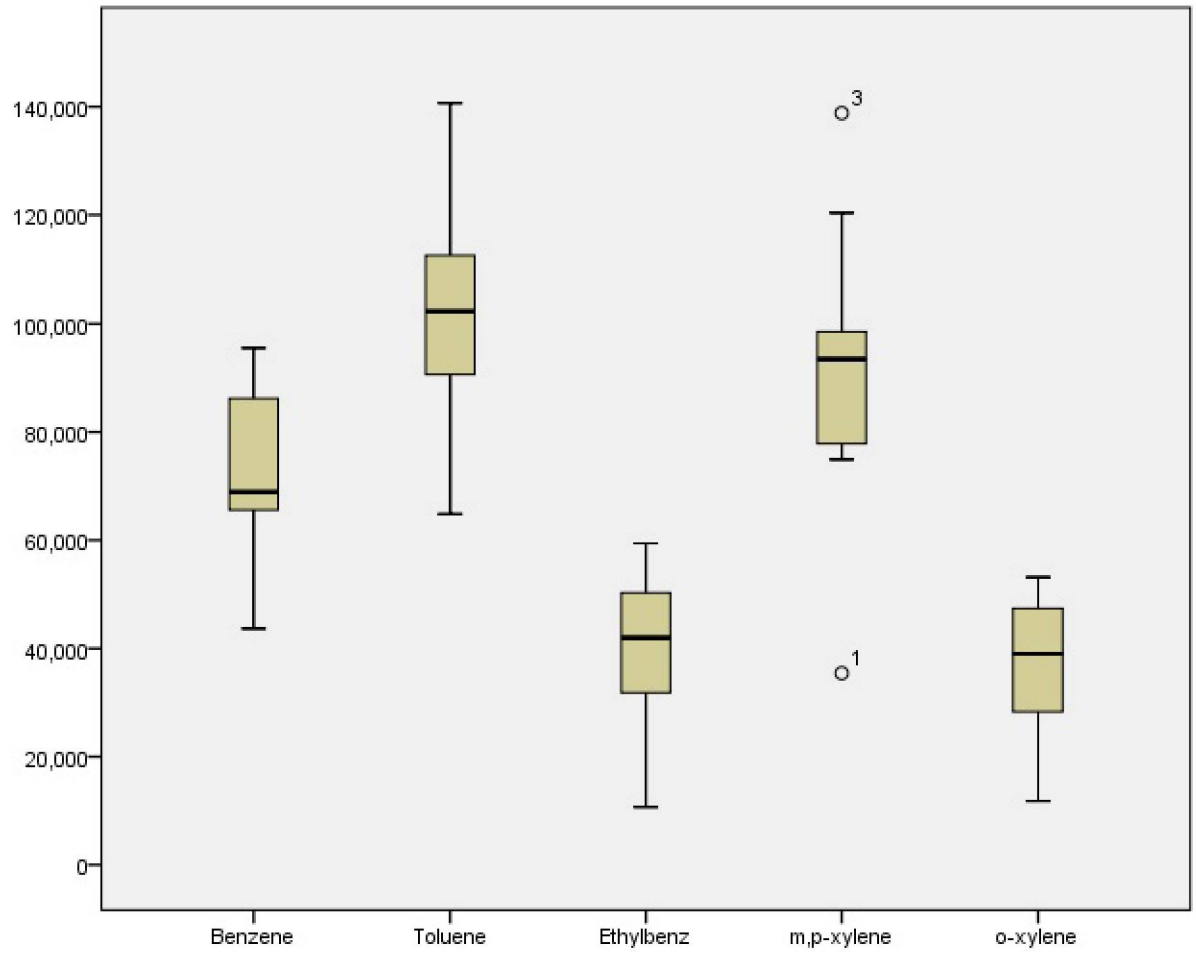
5.9 LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTIFICATION (LOQ) OF BTEX

One of the methods proposed by the ICH (GUIDELINE, 2005) for the calculation of the detection limit consists in the calculation of the the standard deviation of the response based on the standard deviation of the blank: measurement of the magnitude of analytical background response is performed by analyzing an appropriate number of blank samples and calculating the standard deviation of these responses.

The analytical targets of each sample were analyzed each day at the beginning of the analysis process. The results of the areas of each target are presented in FIGURE 29. This figure shows the distribution of the areas obtained by chromatographic analysis for the analytical targets. Their areas are very small, which makes it impossible to calculate from these targets, as it would be reaching inadmissible concentrations (negative).

For example, for the target of Ethylbenzene the average area obtained from the chromatographic analysis corresponded to 40284, which corresponds to a standard deviation of 15579. The ***t*** value for the number of targets analyzed corresponded to 2.8214, with these values the detection limit calculated, in units of concentration, according to TABLE 16, corresponded to -10.9160 μg·ml^{-1}, this negative value of detection limit was presented for all BTEX when starting from the calculation of the standard deviation of the values of the analytical target, reason why this procedure was not used for the determination of the limit of detection.

FIGURE 29 – Box Plot Blank of calibration curves BTEX



SOURCE: Author

According to numeral 8.2.1.3 of the DOQ CRGCRE-008 5a Revision guide (ACREDITAÇÃO, 2016), the concentration of LOQ is always equal to or greater than the first point of the analytical curve. For trace-level analysis, it is recommended to adopt LOQ as the lowest concentration of the analytical curve. In this case, it is essential to include a control in the method, in a concentration equivalent to the LOQ, to follow the performance in this concentration and to provide data for the periodic re-estimation of the same with the control data. The TABLE 28 illustrated that the lowest concentration of the analytical curve was 1.9731 μg·ml^{-1} for Benzene, 1.9556 μg·ml^{-1} for Toluene and 1.9498 for Ethylbenzene, m,p-Xylene and o-Xylene, Consequently, the detection limit for all BTEX are illustrated in TABLE 27.

In our case, the minimum concentration standard was 1.9731 μg·ml^{-1} for Benzene, and the determination of the signal-to-noise ratio was made from it and for each of the constituent BTEX compounds.

In order to make comparisons between the Limits of Detection (LOD) reported in the literature (see TABLE 9) for environmental samples extracted by thermal desorption

TABLE 27 – Limit of Detection BTEX (LOD)

Blank	**Benzene**	**Toluene**	**Ethylbenz**	**m,p-xylene**	**o-xylene**
LOD = [Con. Min]/3.3	0.5979	0.5926	0.5958	0.5958	0.5958
LOQ [Con. Min]	**1.9731**	**1.9556**	**1.9498**	**1.9498**	**1.9498**

TABLE 28 – Limit of quantification (LOQ)

Benzene	Toluene	Ethylbenzene	m-Xylene	o-Xylene	specifications
1.9731	1.9556	1.9498	1.9498	1.9498	(μg·ml^{-1})

and analyzed by chromatography, the injected mass of the lowest concentration standard was calculated. We found that the lower mass detected in the present study, 0.002 μg (1.97 ng), is lower than that reported in studies such as Du et al. (2013), however, the studies reported by Liaud et al. (2014), Pandey and K.-H. Kim (2009b) and Y.-H. Kim and K.-H. Kim (2012) show limit detection much lower than the order of pg, and therefore, it will be necessary more future studies that explore the improvements in the analytical technique to determine lower limits of detection.

5.10 PRECISION OF BTEX

The precision of an analytical procedure is usually expressed as the variance, standard deviation or coefficient of variation of a series of measurements (CV), The CV is usually expressed in %, also known as relative standard deviation (RSD), is calculated as follows:

$$CV = \frac{s}{|\tilde{x}|} * 100 \tag{5.3}$$

Being:

- ***s*** is the standard deviation;
- $\tilde{x}$ is the mean concentration determined

TABLE 29 and TABLE 30 illustrated a relative standard deviation for BTEX in Curitiba. By not depending on the units, this measure has the advantage of allowing to compare the variability of groups of observations given in different units, or of different orders of magnitude. The coefficient of variation is also known by the acronym RSD (from English, standard deviation ratio). The results illustrated in TABLE 29 and TABLE 30 show the excellent precision obtained for the Benzene and Toluene standards, while for the m, p-Xylene and o-Xylene standards, lower precision was found,

and consequently greater deviations. The results are comparable to those obtained in TABLE 12 concerning studies carried out in different parts of the world.

TABLE 29 – Precision BTEX Low Range

Compunds	Stock (μg·ml^{-1})				
	2	10	30	50	70
Benzene	4.96	2.03	3.42	1.17	2.01
Toluene	1.22	4.87	6.35	3.06	0.58
Ethylbenzene	6.75	9.34	4.79	6.35	1.19
m,p-Xylene	4.05	13.73	9.20	0.38	0.87
O-xylene	5.47	14.37	9.25	3.49	5.64

TABLE 30 – Precision BTEX High Range

Compunds	Stock (μg·ml^{-1})				
	90	150	200	250	300
Benzene	1.15	2.18	0.92	1.68	1.29
Toluene	2.50	2.38	0.53	0.09	0.88
Ethylbenzene	4.69	1.18	1.20	0.09	2.36
m,p-Xylene	14.18	1.87	0.44	2.71	1.85
O-xylene	1.36	1.06	5.48	0.27	1.53

To determine the precision of the method, we calculated the coefficient of variation (CV) of the analytical repetitions of each of the injected standards. A lower coefficient of variation represents a lower dispersion of the readings of each standard, which is why it represents a better precision. The data reported in the literature, illustrated in TABLE 12 allows comparisons with the data obtained in the present study (see TABLE 29 and TABLE 30). Of the mean values obtained in the present study, the best precision obtained with respect to CV values is highlighted in the following studies: Ras-Mallorquı, Marcé-Recasens and Borrull-Balların (2007), Du et al. (2013) and C. Cocheo et al. (2009). However, as it happened in the other validation parameters, the data obtained by Liaud et al. (2014), register better precision than those reported in the present study. Likewise, Y.-H. Kim and K.-H. Kim (2012) found better precision when reporting CV 2.0% values for all BTEX analyzed.

In a general way, comparing our study with the literature, we found that the compound that presented the best precision both in the present study and in literature, corresponds to Toluene, while the literature reports higher CV, and therefore lower

precision for Benzene; however, our study, the lower precision of BTEX correspond with o-Xylene.

The greatest variations registered in the Coefficient of Variation (CV) and therefore in the Precision corresponded to the Xylene compounds, both for the low concentration range and for the high concentration range. The reported data of uncertainty for the Radiello sampler (see TABLE 12) are associated precisely with the Xylenes compounds (m, p-Xylene and o-Xylene). This result is consistent with what is illustrated in FIGURE 21, where it is evident that when performing the repetitions for each of the standards used in the calibration curve, the greatest dispersion (amplitude of the box diagram) was recorded for m, p -Xylene and for o-Xylene.

The chromatogram illustrated in FIGURE 26 also allows us to clearly observe how the greatest variations in both the intensity of the peak and in its width, as a function of the retention time corresponded to the Xylene compounds (m, p-Xylene and o- Xylene). Therefore, the high uncertainties associated with the sampling of Xylenes, as well as their dispersion at the time of analysis and chromatographic identification, justify the high variation coefficients presented in TABLE 29 and TABLE 30, and, consequently their lower precision. This information is also corroborated by literature data, such as Pandey and K.-H. Kim (2009b)(14% for m,p xylene), Ezquerro et al. (2004) (11.10% for m,p xylene) and C. Cocheo et al. (2009) (9.1% for m,p xylene), who report the greatest variations in CV for m, p-Xylene and o-Xylene. These values justify that CV values of the order of 14%, such as the one show in TABLE 30, are admissible for the validation process.

5.11 SIGNAL TO NOISE RATIO

This approach can only be applied in analytical procedures presenting baseline noise. The signal-to-noise ratio is determined by comparing the measured sample signals with low known concentrations of the analyte and the white noise of samples by defining the minimum concentration at which the analyte can be detected with confidence.

A signal-to-noise ratio of 10:1, 3: 1 or 2: 1 is generally considered acceptable for estimating the detection limit. It is important to note that the white noise region must be the same as the measured signal. In our case (see TABLE 31), a signal-to-noise ratio well above 10 for all BTEX was found in the gas chromatography analysis using the SIM (Single Ion Monitoring) mode, which means that it is an acceptable ratio for the determination of the detection limit of the method.

TABLE 31 – Ratio Signal / noise

Ratio	Benzene	Toluene	Ethylbenz	m,p-xylene	o-xylene
Signal/noise	2037.07	2596.68	2657.22	3081.09	2179.77

5.12 ROBUSTNESS

The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage.

Examples of typical variations are:

- Stability of analytical solutions;
- Extraction time.

In the case of gas-chromatography, examples of typical variations are:

- Different columns (different lots and/or suppliers);
- Temperature;
- Flow rate.

Understanding the existence of considerable variability in the process of adding standard to the Radiello passive cartridges; this process was carried out by means of automatic injection. For this, the Claurus 680 Perking Elmer chromatograph automatic injector will be used, and the injection was planned in the following manner:

1. Calibration curves shall be obtained by gas phase injection of methanol solutions of the target compounds into preconditioned cartridges. The injections are made through a GC injector, where a short piece (10 cm) of a column without a deactivated coating of large diameter (0.53 i.d.) is installed. The other end has a Swagelock reduction connection (1/16 "- 1/4"). The 1/4 "Swagelock nut must be equipped with a PTFE ferrule instead of the original steel ferrule (use PTFE ferrules that come with the Turbomatrix lids).
2. Injection of 1 μl of a liquid standard containing each of the BTEX concentrations of the calibration curve.
3. The injector was set at 200℃ in order to promote the volatilization of the liquid standard.

4. Once the standard was injected, it was returned to a stream of Helium 5.0 in order to be dragged to the cartridge containing the absorbent. Carbography 4 to do this, the injector for a flow of 50 ml·min^{-1} for two minutes, followed by a flow of 2 ml·min^{-1} for one minute.

5. Once this analyte dragging program was finished, the cartridge was placed in the thermo-desorption equipment, following the same plan of temperatures, times and periods for both patterns and samples.

6. A series of tests were carried out to establish the ones that are most suitable for each stage, as well as the times and pressures.

7. In terms of robustness, it was identified that the variation in each stage of the **thermo desorption** system generated the significant variations in the areas of the peaks of the chromatograms of each standard, affecting the ideal work conditions for the stages: desorption of the cartridge sample (primary desorption), desorption of the sample from the concentration system (secondary desorption) and conditions of the gas chromatograph and the mass detector for the analysis.

8. Regarding the chromatographic analysis, the separation column was Restek Rxi-241 Sil MS, which is a column with selectivity for BTEX and specific for mass detector analysis.

9. The desorption program of the column was obtained from the literature for the mass detector, performing a series of tests to obtain the maximum sensitivity, in terms of the areas of each peak and the separation between them.

10. The quantification of the analyte with the mass detector was obtained by selecting the Single Ion Monitoring mode (SIM), to have a selectivity of each standard. The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. So, we used the primary ion for quantitation and the secondary ions for confirmation of the collection based on their retention times.

11. The programming of the detector in terms of source temperature and the transfer line, as well as the energies of the electronic system, the emission of the source and the optical system (Repeler and Lens) were established from the reported data in literature, and a series of tests carried out in the air quality laboratory of the Federal University of Paraná, Polytechnic center.

6 CONCLUSIONS

The thermal extraction technique of passive samplers from the Radiello Company was established using gas chromatography with mass spectrometry detector (Perkin Elmer Clarus 680), following the EPA TO 15 method.

For this purpose, we optimized the methos of injection systems of calibration standards, the thermal desorption system (primary and secondary desorption), the chromatographic separation conditions of the GS-MS, and the mass detection system. All of these parameters were adjusted for the validation of the analytical method, object of the present investigation.

The production of the calibration standards using the adsorbent tubes was optimized based on the automatic injection of calibration standards, eliminating the manual injections. The final conditions for the injection system was the temperature of the injector (200℃), the initial flow (50 ml·min^{-1} for 2 minutes), and the final flow (2 ml·min^{-1} for 1 minute).

The most efficient desorption flow extraction with the best repetitiveness was 100 ml·min^{-1}.

The trap in the secondary desorption step was set from 10℃ to 325℃ in a few seconds. To optimize flow conditions in the secondary desorption, the pressure constant at 14.8 psi was used so that the flow in the gas chromatograph would not be affected.

The validation of the working range, linearity, sensitivity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy were estimated. The results found in this work showed better sensitivities, LOD, LOQ than other studies.

Finally, to understand the magnitude of the response obtained by the analytical methodology we used, the signal-to-noise ratio was evaluated, which allowed us to establish whether there was a variance in the response level (signal) expressed as a function of the area of the peaks in the chromatogram and its baseline. Significant differences that allow us to clearly differentiate a peak from its noise or baseline, by defining a noise signal value of 10, is accepted. Any value above this represents a clear peak definition. The values in our study are higher than 2000, which undoubtedly shows the suitability of the analytical technique implemented to identify BTEX.

During the development of the our study we only used methanol as solvent and in minimum amounts, reason why this research is considered consistent with the purpose of performing environmentally clean chemical analysis processes.

In conclusion it is also necessary to mention that the thermal desorption tech-

nique with GC-MS chromatographic analysis is not an economical technique, since the Radiello absorbent tubes are expensive and the gas used as trawl gas (Helium) is especially expensive in Brazil, however , during the development of the present investigation it was observed that the Radiello tubes are reusable and that their absorption efficiency does not decrease with the small number of times used, which makes this sampling system require a high initial cost, but the reused of them allows to cushion the initial cost.

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